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Ground-Based Smoke Sampling Techniques Training Course and Collaborative Local Smoke Sampling in Saudi Arabia

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Abstract

Smoke and gaseous emissions such as those generated by multiple oil-well fires can significantly impact the health of the local population. To assess the immediate risk to public health, the chemical and physical properties of the smoke and gaseous emissions must be quickly characterized. Local sampling via portable gas analyzers, filters and pumps, and particle sizing instrumentation provides real-time characterization of pollutant levels.

The Ground-Based Smoke Sampling Techniques Training Course and Collaborative Local Smoke Sampling project was initiated between the Ministry of Defence and Aviation (Kingdom of Saudi Arabia) and the National Institute of Standards and Technology (USA) to train Saudi medical personnel. A team of Saudi and NIST researchers assembled in December 1992 to collect smoke and gas samples in Saudi Arabia for analysis. Sample analysis included determination of polycyclic aromatic hydrocarbons (PAHs), CO, CO₂ and total particulate concentrations. Split-sample analysis was conducted with some samples being analyzed in Saudi Arabia and other samples being returned to NIST for more specialized analysis, including micro-Raman, laser micro-probe, and environmental scanning electron microscopy.

These analyses provide a snapshot of the physical and chemical properties of the aerosols sampled in Saudi Arabia, but due to the very limited number of samples, they do not provide a reasonable basis for estimating the short- or long-term health risk due to exposure to smoke and gaseous emissions. Concentrations of PAHs measured in the samples were about the same order of magnitude as samples collected in Roanoke, Virginia, but 3 to 10 times lower than samples from Boise, Idaho. While these results do suggest significant levels of PAH and dust particulates, the data set is very limited and a program involving the collection and analysis of air samples in or around Saudi Arabian urban areas would provide valuable data for determining current airborne PAH concentrations as well as for devising air pollution control strategies for the future. The appearance of significant concentrations of PAHs in what was expected to provide background levels indicates that a more comprehensive sampling program should be implemented to characterize the levels and the distribution of PAHs throughout the Kingdom.

TABLE 1		TABLE 2	
Summary of the results of the regression analysis		Summary of the results of the regression analysis	
Variable	Dependent variable	Variable	Dependent variable
Age	Dependent variable	Age	Dependent variable
Gender	Dependent variable	Gender	Dependent variable
Education	Dependent variable	Education	Dependent variable
Income	Dependent variable	Income	Dependent variable
Health	Dependent variable	Health	Dependent variable
Marital status	Dependent variable	Marital status	Dependent variable
Religion	Dependent variable	Religion	Dependent variable
Political affiliation	Dependent variable	Political affiliation	Dependent variable
Occupation	Dependent variable	Occupation	Dependent variable
Home ownership	Dependent variable	Home ownership	Dependent variable
Travel frequency	Dependent variable	Travel frequency	Dependent variable
Volunteering	Dependent variable	Volunteering	Dependent variable
Charitable giving	Dependent variable	Charitable giving	Dependent variable
Political participation	Dependent variable	Political participation	Dependent variable
Community involvement	Dependent variable	Community involvement	Dependent variable
Environmental concern	Dependent variable	Environmental concern	Dependent variable
Healthcare usage	Dependent variable	Healthcare usage	Dependent variable
Food consumption	Dependent variable	Food consumption	Dependent variable
Energy usage	Dependent variable	Energy usage	Dependent variable
Waste management	Dependent variable	Waste management	Dependent variable
Transportation mode	Dependent variable	Transportation mode	Dependent variable
Shopping frequency	Dependent variable	Shopping frequency	Dependent variable
Exercise frequency	Dependent variable	Exercise frequency	Dependent variable
Alcohol consumption	Dependent variable	Alcohol consumption	Dependent variable
Tobacco use	Dependent variable	Tobacco use	Dependent variable
Substance use	Dependent variable	Substance use	Dependent variable
Stress levels	Dependent variable	Stress levels	Dependent variable
Mental health	Dependent variable	Mental health	Dependent variable
Physical health	Dependent variable	Physical health	Dependent variable
Life satisfaction	Dependent variable	Life satisfaction	Dependent variable
Overall well-being	Dependent variable	Overall well-being	Dependent variable

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1.0 Introduction

Large quantities of smoke and gaseous emissions such as those generated by multiple oil-well fires can significantly impact the health of the local population. In order to assess the immediate risk to public health, it is important to characterize quickly the chemical and physical properties of the smoke or gas plume. Local sampling via portable gas analyzers, filters and pumps, and particle sizing instrumentation can provide real-time characterization of pollutant levels which are affecting a small and localized population. Short-term exposure to high levels of smoke and gaseous emissions often exacerbate certain medical conditions, such as asthma or emphysema. Exposure to high levels of smoke and other airborne particulates can cause pneumoconiosis which reduces the lungs' efficiency [1]. Other combustion products, such as sulfur dioxide and nitrogen dioxide, are lung irritants; and pulmonary edema can result from exposure to high concentrations [2]. Relatively short-term exposure, 1 to 5 minutes, to carbon monoxide [3,4] or carbon dioxide [5,6] at 1.5% and 15% levels, respectively, can lead to unconsciousness and death via asphyxiation. Portable gas analyzers and other particulate sampling instrumentation allow the concentration of aerosol particulates and gases to be quickly determined. Once the smoke or gaseous emissions have been characterized, knowledgeable medical specialists can recommend appropriate action, such as remaining indoors, wearing filter masks, and/or evacuating the affected area.

Local monitoring of smoke and gas concentrations is critical to the real-time assessment of acute exposure of local population groups, but meteorological modelling and source characterization are usually necessary to provide health warnings over longer time frames for larger areas. Routine sampling and monitoring programs are necessary for evaluating longer term exposures. Both acute and chronic exposures need to be quantified to assess completely the health impact of the smoke and combustion gases.

In 1991, during the oil-well fires in Kuwait, the Ministry of Defence and Aviation (Kingdom of Saudi Arabia) decided to start training some of their medical personnel in the operation of portable gas analyzers and particulate sampling instrumentation. This training would allow the Saudi medical personnel to begin local sampling of smoke and gases in Saudi Arabia as the oil wells burned in Kuwait. Local monitoring of smoke and gas concentrations was the just the first step in collecting some of the data necessary for qualified medical specialists to assess the risk to the local population. Since the National Institute of Standards and Technology (NIST) had an ongoing program to study the smoke and gaseous emissions from crude oil fires [7 - 13], the Ministry of Defence and Aviation (MODA) proposed that NIST provide the training for Saudi personnel via a Ground-Based Smoke Sampling Techniques Training Course and Collaborative Local Smoke Sampling in Saudi Arabia project. The two week training course occurred at NIST in August 1992 and involved lectures and demonstrations of gravimetric measurements, light scattering cells, portable size classifiers, battery-powered gas analyzers, and filter sampling trains. NIST's Organic Analytical Research Division demonstrated sample preparation and illustrated the use of gas and liquid chromatographic instrumentation.

A team of MODA and NIST researchers assembled in December 1992 to collect smoke, and gas samples in Saudi Arabia for analysis. Analysis of smoke and gas samples included determination of polycyclic aromatic hydrocarbons (PAHs), CO, CO₂ and total particulate concentrations. Split-sample analysis was conducted with some samples being analyzed locally and other samples being returned to NIST for more specialized analysis, including micro-Raman, laser micro-probe, and environmental scanning electron microscopy. The performance of the portable analyzers in the field was verified by comparing the concentrations measured in the field with the samples analyzed in the laboratory.

2.0 Ground-Based Smoke Sampling Training Course

This course was designed to introduce MODA medical personnel to techniques for ground-based monitoring of acute episodes of smoke and gaseous emissions. Topics presented included total particulate concentrations, inhalable particulates, gas analyzers, gas sampling, hydrocarbon monitoring, metals and inorganic compound detection, and analytical chemistry. A more detailed list of topics is presented in Appendix A.

2.1 Total Mass Concentration and Inhalable Fraction of Particulates

In estimating the impact of smoke on a local area, it is important to determine the total mass concentration of particulates suspended in the air. In the field, total mass concentration of aerosols can be measured using light-scattering instruments or gravimetric techniques. Real-time concentrations of total particulate material are quickly obtained using portable light-scattering cells. Light-scattering cells, such as the Mini-Ram*, are battery powered and provide digital or analog output of real-time total aerosol concentrations. The smoke passes through a light cell where the intensity of scattered light is monitored. The scattering intensity increases as the concentration of the particulates increases. Scattering cells can be calibrated for specific concentration ranges, although the cells are unable to differentiate between smoke particulates and sand or soil particles. While the light-scattering cells can provide immediate measurements of particle concentrations, the somewhat slower gravimetric method can yield more accurate data and also provides a filter sample for additional analyses.

The gravimetric method of determining the total particulate concentration involves using a portable battery-powered pump to pull a known volume of smoke through a pre-weighed filter. The filter sample is typically returned to a laboratory and re-weighed to determine the total particulate mass. Dividing the particulate mass by the total volume sampled provides the total particulate concentration. The gravimetric filter method collects aerosol particulates over a wide range of particle sizes and concentration while the light scattering cells typically are typically optimized for a specific (usually relatively narrow) size and concentration range. Thus the gravimetric techniques can provide more accurate total particulate concentrations, but can not provide them in real-time. Gravimetric techniques can not differentiate between background soil aerosols and fire generated smoke so other more specialized analyses are needed to determine whether the particulates originated in the soil or from fuel combustion.

If the total mass concentration of particulates suggests that there might be enough particulates to be a significant hazard to the population, then it becomes more important to determine the inhalable fraction of the particulates. The particulate size is important because the smaller the particle the further the particle typically penetrates into the human respiratory system. Relatively large particles, approximately 7 to 10 μm in diameter, may be filtered out by the nose or throat, while

* Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

smaller particles, about 0.4 to 1.1 μm in diameter, may travel through the bronchi and reach the alveolar spaces of the lung. The inhalable particulates, usually less than 10 μm in diameter, can be monitored by cascade impactors or ambient samplers equipped with a size selective sampling head.

Cascade impactors are available in either completely portable models, such as the Marple Personal Sampler or less portable versions, including the Andersen 2000 Impactor. The less portable versions usually require larger pumps which are more difficult to power with batteries. A cascade impactor aerodynamically classifies the smoke aerosol as the particulates are pulled through a series of stages. As the aerosol cascades through the stages the larger particulates are inertially impacted onto the early stages while smaller particles continue to be drawn through additional stages. As the carrier gas is accelerated between each stage, the largest of the remaining particles are impacted on subsequent stages, gradually distributing the aerosol particles on the stages as a function of aerodynamic particle size. Typically, each impactor stage simulates how far an aerosol particle could travel into the respiratory system. For instance, particulates captured on the first stage may be filtered out by the mouth or nose while particles collected on the eighth stage may penetrate deep into the lung. As with the gravimetric filter measurements, the individual stages of a cascade impactor must be weighed before and after sample collection. Since weighing the individual stages in the field is difficult, the stages are usually weighed before going into the field and after returning from the field. After weighing each stage, it is placed into a sample carriers which can be sealed. Once in the field, the stages are unpacked, loaded into the impactor, and the samples collected. The impactors are then unloaded, resealed, and placed on dry ice for transport to the laboratory.

Ambient samplers, such as the PM-10 HiVol, are equipped with a sampling head which allows only inhalable particles to be collected on the filter. Since ambient samplers are designed to monitor relatively low concentrations of aerosol particles, the equipment must sample very large volumes of air. While the personal cascade impactor samples 1 to 2 liters per minute, the PM-10 HiVol collects 1000 to 1500 liters per minute. The PM-10 HiVol sampler is relatively large and not very portable, but it does allow routine monitoring of inhalable aerosol mass concentrations. PM-10s are often used to establish background or ambient aerosol levels. The PM-10s are also used to monitor emission sources to help insure compliance with aerosol emission regulations.

2.2 Gas Analyzers and Gas Sampling

In estimating the impact of gaseous emissions on a local area, it is also important to determine the chemical composition of the smoke plume or gas cloud. A limited number of gas species can be identified in real-time via portable battery-powered analyzers utilizing electrochemical sensors. The species which can be monitored include sulfur dioxide (SO_2), nitrogen dioxide (NO_2), hydrogen sulfide (H_2S), carbon monoxide (CO) and carbon dioxide (CO_2). Multi-gas analyzers incorporate small sample pumps while single-gas instruments typically use diffusion cells.

Additional gases can be identified by collecting a sample in a container and returning the sample to a laboratory for analysis by gas chromatography. The container may be simply an evacuated cylinder or may be a small glass tube filled with sorbent material designed to select specific species. Evacuated sample containers range from electro-passivated stainless steel cylinders with calibrated flow controllers to Tedlar plastic bags with off/on valves. Sorbent materials such as XAD-2, silica gel, Tenax, or coconut charcoal will preferentially adsorb or absorb specific species. A portable pump can be used to collect or "grab" samples to fill Tedlar bags with 3 - 5 liters of smoke and/or combustion gases. Evacuated stainless steel containers, such as Summa cylinders, can collect samples with or without a pump. The portable pump is also used to pull a known volume of aerosol through

the sorbent tubes. Sample bags, Summa cylinders, or sorbent tubes are returned to a laboratory for subsequent analysis with gas chromatography. These "grab" samples, where a sample is collected in the field but returned to the laboratory, offer more accurate measurements, but do not provide the real-time data of a portable gas analyzer.

2.3 Hydrocarbon Monitoring

Another component of the smoke emissions from many combustion sources is the hydrocarbon fraction. This portion of the emissions can range from unburned fuel, usually lighter hydrocarbons, volatile organic compounds (VOCs), to polycyclic aromatic hydrocarbons (PAHs). Since some of the PAHs are thought to be mutagenic, it is especially important to identify and quantify these compounds. Unfortunately, portable hydrocarbon analyzers can not detect or discriminate these compounds rapidly enough to provide real-time concentrations. A limited number of the lighter hydrocarbons, such as methane or propane, can be detected in real-time using portable analyzers. Hydrocarbon samples can be collected by using small portable pumps to fill evacuated stainless steel cylinders or Tedlar plastic bags, but the higher molecular weight compounds may condense on the walls of the container. Careful warming of the containers during the analysis procedure can re-volatilize some of the compounds. Unfortunately, the condensation of the heavier hydrocarbons introduces additional uncertainty into the concentration measurements.

An alternative analytical technique for both the light and heavy hydrocarbons is to use a portable pump to pull a known volume of smoke through a pre-weighed filter and/or sorbent tube which is returned to a specialized laboratory for the measurement of PAHs and VOCs. For either grab samples or sorbent tubes, the specialized techniques which are often used to determine hydrocarbon concentrations include gas chromatography and liquid chromatography. Operators with the background and training necessary for these specialized analysis techniques can usually be found at large hospitals, universities, or private and government research centers.

2.4 Inorganic Components

Another component of a smoke plume can be various inorganic elements and compounds including metals, sulfates, and nitrates. The metals and sulfates are often produced by the combustion of fuels containing trace metals and/or sulfur. Nitrates and sulfates can result from the reaction of oxides of sulfur or nitrogen with other compounds in the high temperature fire environment. However, the combustion process is not the only path that inorganic compounds may take to become part of the smoke plume. The convective flow patterns associated with the fire plume can entrain the surrounding air into the fire. Fine dust or soil can be swept into the fire and emerge in the smoke plume. In order to identify and determine the concentrations of these chemical species, a known volume is pulled through a filter and returned to the lab for analysis. Specialized analysis techniques include laser microprobe mass spectrometry, micro-Raman analysis, environmental scanning electron microscopy, neutron activation, and ion chromatography.

3.0 Collaborative Local Smoke Sampling in Saudi Arabia

Mr. Nelson P. Bryner and Dr. Bruce A. Benner, Jr. of NIST visited Saudi Arabia to tour research facilities at the Riyadh Armed Forces Military Hospital (RAFMH) and collect smoke and gas samples. RAFMH is the largest military hospital in Saudi Arabia and has extensive research facilities. Like all military hospitals in Saudi Arabia, RAFMH is administered by the Ministry of Defence and Aviation. Lt. Colonel Ibrahim Al-Nasser hosted the visit and arranged for the sampling trips to Dhahran and Al-Jubail.

3.1 Riyadh Armed Forces Military Hospital

The tours of the Riyadh Armed Forces Military Hospital (RAFMH) were presented by Mr. Abdulrahman Al-Asmari, Captain Suleimun Al-Hedaithy and Lt. Colonel Al-Nasser. The Saudi hosts provided a tour of the Toxicology, Biochemistry, Clinical Pathology, Endocrinology and Environmental Aerosol Laboratories. The NIST researchers were quite impressed by the size and the sophistication of the RAFMH laboratory facilities. The tour of the Toxicology Laboratory was particularly valuable, since this department has some of the equipment necessary for measurement of organic and inorganic air pollutants. The gas chromatograph (GC), the gas chromatograph with mass spectrometric detector (GC-MS) and the atomic absorption spectrophotometers in the Toxicology Laboratory could be used for future measurement of organic and inorganic constituents of air particulate matter collected in Saudi Arabia. The polycyclic aromatic hydrocarbons (PAHs) are of interest in the atmosphere since they are used as indicators of combustion processes and a number of PAHs are considered to be mutagenic. Some additional equipment, including specific GC capillary columns, and time for method development would be necessary before actual sample analysis (for PAHs) could be accomplished. In addition, NIST has available a large number of Standard Reference Materials (SRMs) that should be used for quality control and quality assurance of the analyses. Procurement of a new gas chromatograph with combined Fourier Transform Infra-Red and Mass Spectrometric Detection capability would be desirable since the two detection techniques compliment one another and aid in analyte confirmation. The enthusiasm and interest expressed by the RAFMH hosts suggested that they are prepared to put forth the effort necessary in establishing a high quality program for monitoring health-related compounds in the atmosphere.

Mr. Bryner and Dr. Benner were pleased to discuss the purpose of their visit with Brigadier General Ahmed Moaz, Director of Laboratory Services, Major General Dr. Ketab Al-Otaibi, Director of Riyadh Armed Forces Military Hospital and with Major General Dr. Abdulhameed Al-Fraidie, Director of Medical Services Department (MSD), Ministry of Defence and Aviation. All of the discussions, especially with Dr. Al-Fraidie, indicated a need and desire for the MSD to continue development of the technical expertise and facilities necessary to assess the impact of environmental aerosols and particulates on the health of the Saudi people. Lt. Colonel Al-Nasser, Captain Al-Hedaithy, Lieutenant Abdullah Kholaify and Mr. Al-Asmari already form the core of an environmental aerosol assessment center. Additional personnel will be required as more comprehensive sampling and analysis are implemented. While the present Toxicology Laboratory can, with minor additions, provide the facilities necessary for initial analysis, the laboratory will have to be expanded to support a comprehensive environmental aerosol monitoring program.

3.2 Collaborative Sampling - Field Work

On Saturday, December 5, 1992, the four hosts from RAFMH and the two NIST guests travelled to Dhahran to collect air samples for subsequent analyses by NIST and RAFMH. Samples were collected at the King Fahad Military Medical Center (KFMMC) near Dhahran and at the Royal Saudi Naval Base (RSNB) near Al-Jubail (Tables 1 to 5). Samples collected at KFMMC were expected to represent background air samples while those collected at the RSNB were expected to be highly concentrated in organic pollutants from the heavy industrial sites near the city of Al-Jubail. A number of inhalable particulate matter samples (PM-10), particle size distribution samples (Marple Cascade Impactor), PAH sampling trains (Teflon filter and XAD sorbent tube), organic/inorganic carbon analysis samples (Quartz filter) and microscopy samples were collected at both sites (Table 1 - 5). One PM-10 sample was collected at each of three sites, including the roof of the main hospital at KFMMC, the roof of apartment building 74 at KFMMC, and the roof of the hospital at RSNB. Two sets of PAH sampling trains including a 35 mm Teflon filter in line with a XAD-2 air sorbent tube were collected at the KFMMC apartment building and the RSNB. The KFMMC apartment building sample was collected during a dust storm, and the associated filter had an easily observable amount of "reddish-tan" sandy material on its surface. A field blank was also generated by sampling indoor apartment air through a sampling train for two minutes. A sealed XAD-2 cartridge from the same lot as those used for the outdoor sampling was employed as the laboratory blank for that media. This was necessary because unlike the filter material, which is pre-cleaned by either heating ($> 500^{\circ}\text{C}$) or extracting with dichloromethane, the XAD-2 sorbent tubes were used as received from the vendor, and it was of interest to distinguish contamination inherent in the XAD sorbent from any obtained in the field.

During the field work, instrument hardware assembly, operation, and calibration as well as site selection considerations, were discussed with the RAFMH personnel. They successfully demonstrated their ability to assemble and calibrate PAH sampling trains, personal cascade impactors, PM-10 HiVol Samplers, and single- and multiple-gas analyzers. All the sampling equipment performed satisfactorily and a number of the samples were noticeably high in collected particulate matter. The group returned to Riyadh on December 9.

4.0 Sample Analysis

The samples were divided between RAFMH and NIST to allow for split-sample analysis. Samples left in Riyadh for analysis included PAH-02, PAH-03, XAD-02, XAD-03, Q-02, Q-06, and B-07. Each of the PM-10 samples was divided in half with each laboratory receiving a filter half for analysis. The electron microscopy samples, and personal cascade impactor samples were all returned to NIST for analysis.

At NIST, the PAH samples (Teflon filter and XAD-2 sorbent tube), quartz filters, and PM-10 samples were analyzed for polycyclic aromatic hydrocarbon content. Quartz fibers from the PM-10 samples and particles from the cascade impactor stages were examined by Laser Microprobe Mass Spectrometry. Other particles selected from cascade impactor stages were investigated using Micro-Raman Analysis. Environmental Scanning Electron Microscopy was employed to study XAD adsorbent, PM-10 filters, and impactor stages. Thermal-optical analysis techniques were used on PM-10 filters to determine organic and elemental carbon content. Gas chromatography was used to measure carbon dioxide and carbon monoxide concentrations of the grab bag samples.

Table 1. PAH Teflon Filter Samples

Filter ID	Filter Material and size	Date Collected	Start Time	Stop Time	Total Collection Time (min)	Flow Rate L/min	Total Volume Liters	Sample Mass mg	Collection Location
PAH-01	Teflon 37 mm	7DEC92	1900	2110	130	2	260	- 0.89	RSNB Al-Jubail
PAH-02	Teflon 37 mm	9DEC92	1900	2110	130	2	260	- 0.06	RSNB Al-Jubail
PAH-03	Teflon 37 mm	9DEC92	0637	1105	268	2	536	1.26	KFMMC Dhahran
PAH-04	Teflon 37 mm	7DEC92	1113	1402	175	2	350	- 0.37	KFMMC Dhahran
PAH-05	Teflon 37 mm	9DEC92	0150	0637	291	2	582	1.88	KFMMC Dhahran
PAH-06	Teflon 37 mm	9DEC92	0637	0639	2	2	4	0.05	Dhahran Field Blank
PAH-07	Teflon 37 mm								Lab Blank
PAH-08	Teflon 37 mm								Lab Blank
PAH-09	Teflon 37 mm								Lab Blank
RSNB - Royal Saudi Naval Base Hospital Roof, Al-Jubail KFMMC - King Fahad Military Medical Center Roof and Apartment Roof, Dhahran									

Table 2. PAH Sorbent (XAD-2) Tube Samples

Tube ID	XAD-2 Sorbent Tube	Date Collected	Start Time	Stop Time	Total Collection Time (min)	Flow Rate L/min	Sample Volume Liters	Collection Location
XAD-01	150 mg / 50 mg 8 mm x 110 mm	7DEC92	1900	2110	130	2	260	RSNB Al-Jubail
XAD-02	150 mg / 50 mg 8 mm x 110 mm	7DEC92	1900	2110	130	2	260	RSNB Al-Jubail
XAD-03	150 mg / 50 mg 8 mm x 110 mm	9DEC92	0637	1105	291	2	536	KFMMC Dhahran
XAD-04	150 mg / 50 mg 8 mm x 110 mm	7DEC92	1113	1402	175	2	350	KFMMC Dhahran
XAD-05	150 mg / 50 mg 8 mm x 110 mm	9DEC92	0150	0637	291	2	582	KFMMC Dhahran
XAD-06	150 mg / 50 mg 8 mm x 110 mm	9DEC92	0637	0639	2	2	4	Dhahran Field Blank
XAD-07	150 mg / 50 mg 8 mm x 110 mm							Lab Blank
XAD-08	150 mg / 50 mg 8 mm x 110 mm							Lab Blank
XAD-09	150 mg / 50 mg 8 mm x 110 mm							Lab Blank
RSNB - Royal Saudi Naval Base Hospital Roof, Al-Jubail KFMMC - King Fahad Military Medical Center Roof and Apartment Roof, Dhahran								

Table 3. Total Particulate (TP) Samples

Filter ID	Filter Material and size	Date Collected	Start Time	Stop Time	Total Collection Time (min)	Flow Rate L/min	Total Volume Liters	Sample Mass mg	Collection Location
Q-01	Quartz 47 mm	7DEC92	1900	2110	130	2	260	- 0.35	RSNB Al-Jubail
Q-02	Quartz 47 mm	7DEC92	1900	2110	130	2	260	- 0.29	RSNB Al-Jubail
Q-04	Quartz 47 mm	7DEC92	1113	1406	175	2	350	- 0.69	KFMMC Dhahran
Q-05	Quartz 47 mm	9DEC92	0150	0637	292	2	584	1.63	KFMMC Dhahran
Q-06	Quartz 47 mm	9DEC92	0637	1105	268	2	536	0.59	KFMMC Dhahran
Q-07	Quartz 47 mm	9DEC92	0637	0639	2	2	4	- 0.02	Dhahran Field Blank
Q-08	Quartz 47 mm				Lab Blank				
Q-09	Quartz 47 mm				Lab Blank				
Q-10	Quartz 47 mm				Lab Blank				
RSNB - Royal Saudi Naval Base Hospital Roof, Al-Jubail KFMMC - King Fahad Military Medical Center Roof and Apartment Roof, Dhahran									

Table 4. Inhalable Particulate (IP) Filter Samples

Filter ID	Filter Material and size	Date Collected	Start Time	Stop Time	Total Collection Time (min)	Flow Rate m ³ /min	Total Volume m ³	Sample Mass mg	Collection Location
PM10-01	Quartz 216 x 279 mm	6DEC92	1640	1141	1133	1.2	1348	- 76.4	KFMMC Dhahran
PM10-02	Quartz 216 x 279 mm	7DEC92	1802	1010	965	1.2	1177	68.6	KFMMC Dhahran
PM10-03	Quartz 216 x 279 mm	7DEC92	1901	0721	740	1.2	903	17.8	RSNB Al-Jubail
PM10-04	Quartz 216 x 279 mm	9DEC92	1105	1110	5	6			KFMMC Dhahran Field Blank
PM10-05	Quartz 216 x 279 mm								Lab Blank
RSNB - Royal Saudi Naval Base Hospital Roof, Al-Jubail KFMMC - King Fahad Military Medical Center Roof and Apartment Roof, Dhahran									

Table 5. Grab Bag, Electron Microscopy, and Cascade Impactor Samples

Bag ID	Material and size	Date Collected	Start Time	Stop Time	Total Collection Time (min)	Flow Rate L/min	Total Volume Liters	Collection Location
B-07	Tedlar Bag 4 liter	7DEC92	1900	1902	2	2	4	RSNB Al-Jubail
B-08	Tedlar Bag 4 liter	7DEC92	2110	2112	2	2	4	RSNB Al-Jubail
B-06	Tedlar Bag 4 liter	9DEC92	0637	0639	2	2	4	KFMMC Dhahran
TEM-01	Carbon Coated Copper Grid	8DEC92	1715	2030	195	2	390	KFMMC Dhahran
TEM-02	Carbon Coated Copper Grid	9DEC92	0637	1105	268	2	536	KFMMC Dhahran
MA-01	Stainless Steel Substrates	9DEC92	0150	0637	243	2	582	KFMMC Dhahran
MA-02	Mylar Substrates	9DEC92	0637	1105	268	2	536	KFMMC Dhahran
RSNB - Royal Saudi Naval Base Hospital Roof, Al-Jubail KFMMC - King Fahad Military Medical Center Roof and Apartment Roof, Dhahran Each cascade impactor sample consisted of 7 collection substrates (Stages 1 through 7) which were either stainless steel or Mylar and a polyvinyl chloride backup filter.								

4.1 Polycyclic Aromatic Hydrocarbons Analysis

Contributed by -

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4.1.1 Sample Preparation and Analysis

The PM-10 filter samples and the PAH sampling trains, Teflon filter and XAD-2 sorbent tube, were analyzed for PAHs. Each type of sample, such as PM-10 or Teflon filter, was extracted and analyzed using techniques specifically developed for each sample media. Each sample was "spiked" with internal standards and several Standard Reference Materials with certified PAH concentrations were simultaneously analyzed to provide quality assurance.

Each PAH sampling train consisted of a 37 mm diameter Teflon filter followed by an XAD-2 sorbent tube. The sorbent tube was an 8 mm diameter by 110 mm long glass tube with 200 mg of XAD-2 collections media. The XAD-2 sorbent material was divided into two segments, the upstream (150 mg material) and downstream (50 mg material). Each segment of an XAD cartridge and the associated glass wool was treated as individual samples (two per XAD cartridge sample). Any PAHs detected above blank levels in the downstream XAD segment would indicate that the analytes were not quantitatively collected by the upstream XAD cartridge and experienced "breakthrough." The XAD samples were placed in 15 mL centrifuge tubes, spiked with a solution containing known amounts of perdeuterated PAHs and extracted by ultrasonication for 5 min with 5 mL of dichloromethane (DCM). The extracts were then transferred to clean 15 mL centrifuge tubes, leaving most of the sorbent and glass wool behind, concentrated under N_2 to ≤ 1 mL and filtered through pre-cleaned 0.2 μ m syringe filters. The extracts were further concentrated under N_2 to ≤ 50 μ L prior to instrumental analysis.

The 37 mm Teflon filters associated with the XAD samples were processed by the same procedure as that described above for the XAD samples except that the filters required 20 mL of DCM for the ultrasonic extraction.

The PM-10 filter samples were cut into two equal pieces (one-half left with MODA personnel) and one-half of each filter was spiked with the same perdeuterated PAH standard as were the XAD and Teflon filter samples and soxhlet extracted for 18 h with 300 mL DCM. The extracts were then concentrated to 0.5 mL under N_2 (Turbovap), and filtered through pre-cleaned 0.2 μ m syringe filters.

Standard Reference Material 1491 (Aromatic Hydrocarbons in Hexane/Toluene) was fortified with known amounts of perdeuterated PAHs and processed through the identical extraction procedures as the samples. Response factors generated by running these standards corrected for differences in the recoveries and detector responses between the analytes and the perdeuterated standards. Two samples of Standard Reference Material (SRM) 1649 (Urban Dust/Organics) were processed through the ultrasonic and soxhlet extraction procedures, serving as quality assurance samples.

4.1.2 GC-MS PAH Analysis

The PAHs were detected by mass spectrometry (MS) using a Hewlett-Packard 5970 Mass Selective Detector interfaced with an HP 5890 gas chromatograph (GC). The GC-MS was tuned daily prior to beginning analyses of the samples. From 1 to 2 μL volumes of the prepared extracts and standards were injected onto a 1.5 m retention gap connected to the analytical column used in quantifying the PAH. Each extract was analyzed once. The 5% phenylmethyl-substituted polysiloxane gas chromatographic column (DB-5ms, 60 m x 0.25 mm, 0.25 μm phase) was used at a head pressure of 276 kilopascals (40 psi) helium (linear velocity of 43 cm/s) with a temperature program beginning with a 1 min hold at 100 °C followed by a rapid ramp (60 °C/min) to 150 °C, then a gradual increase (2 °C/min) to 325 °C. The MSD was operated in the selected ion-monitoring mode at an electron multiplier voltage of 1400 V. Specifics of the selected ion-monitoring program are listed in Table 6. The PAHs present in the sample extracts were quantified by peak area comparisons with perdeuterated PAHs spiked into the samples prior to extraction. Response/recovery factors generated as described above, corrected for differences in the recoveries and detector responses between the analytes and the standards. Reconstructed selected-ion chromatograms for one of the XAD, the PM-10 and the Teflon filter samples can be found as Appendices B, C, and D.

4.1.3 Results and Discussion

For quality assurance purposes, Standard Reference Material (SRM) 1649 (Urban Dust/Organics) was processed through both the ultrasonic and the soxhlet extraction procedures described above. Results generated by the two methods, as well as certified concentrations reported in the SRM's Certificate of Analysis, are listed in Table 7. Good agreement was observed between results generated by soxhlet extraction and the certified concentrations. Results for half of the PAHs from the ultrasonic extraction procedure were significantly higher (by $\geq 30\%$) than from the soxhlet technique, perhaps due to problems in the spiking of the internal standard (5 μL volume) and/or inhomogeneity of the SRM at the 5 mg level. The XAD and the Teflon filter samples were spiked at the same 5 μL level as the SRM and the results for those samples may be biased toward higher concentrations.

Table 8 lists the amounts of those PAHs detected in the extracts of the XAD laboratory and field blanks. Naphthalene and benzo[a]pyrene were the only PAHs significantly enriched ($\geq 3\text{x}$) in the field blank over the laboratory blank. Results for the upstream and downstream segments of each of two XAD samples collected at KFMMC and RSNB are shown in Table 9. When appropriate, the results were corrected for field blank concentrations. With the exception of fluorene and dibenzothiophene, the downstream segments of the XAD samples showed little indication of significant breakthrough of PAHs during sample collection. The XAD cartridges would collect both vapor phase PAHs as well as those desorbed from the retained particles. Except in situations of extreme temperatures, such as those experienced during combustion source sampling, one would not expect to observe larger molecular weight PAHs (≥ 228 atomic mass units) on the XAD cartridges. Results for the associated Teflon filter samples and field blank are listed in Table 10. The vast majority of the PAHs were either not detectable or indistinguishable from the field blank contamination levels. As mentioned above, PAH sample train #5 (PAH-05 and XAD-05) collected at KFMMC during a dust storm had observable amounts of reddish-tan dust on the filter. The PAH-05 results displayed in Table 10 suggest that the dust is not a significant source or carrier for airborne PAHs.

Table 6. Mass Spectrometric Selected Ion-Monitoring Program for Determining PAHs in Extracts of Saudi Air Samples

Selected Ion Monitoring Program		
Time (Minutes)	Masses Monitored (amu)	PAHs Determined
5 - 6.8	128, 136	naphthalene, naphthalene-d ₈
6.8 - 8	142	methylnaphthalenes
8 - 12	152, 154, 156	Biphenyl, acenaphthalene, acenaphthene, dimethylnaphthalenes
12 - 16	166, 170, 176	fluorene, trimethylnaphthalene, fluorene-d ₁₀
16 - 22	178, 184, 188	phenanthrene, anthracene, dibenzothiophene, phenanthrene-d ₁₀
22 - 31.5	190, 192, 206	4,5-methylenepheneanthrene, methylphenanthrenes, dimethylphenanthrenes
31.5 - 36	202, 212	fluoranthene, acephenanthrylene, pyrene, pyrene-d ₁₀
36 - 52	226, 228, 240	benzo[ghi]fluoranthene, benzo[c]phenanthrene, triphenylene, benz[a]anthracene, chrysene, benz[a]anthracene-d ₁₂
52 - 70	252, 264	benzofluoranthenes, benzopyrenes, benzo[k]fluoranthene-d ₁₂ , benzo[a]pyrene-d ₁₂
70 - 80	276, 278, 288, 292	indeno[123,cd]pyrene, benzo[ghi]perylene, anthanthrene, dibenzanthracenes, benzo[ghi]perylene-d ₁₂ , dibenz[a,h]-anthracene-d ₁₄

Table 7. Measurement of PAHs in Standard Reference Material 1649 (Urban Dust/Organics) ($\mu\text{g/g}$)

PAH	Ultrasonic Extraction ^a	Soxhlet Extraction ^b	Certified Concentration ^c
phenanthrene	7.48	5.30	
anthracene	1.01	1.32	
4,5-methylenepheneanthrene	0.68	0.35	
3-methylphenanthrene	1.12	0.74	
2-methylphenanthrene	0.68	0.89	
4- and 9-methylphenanthrene			
1-methylphenanthrene	0.98	1.73	
fluoranthrene	9.60	6.53	7.1 ± 0.5
acephenanthrylene			
pyrene	8.59	5.75	
benz[a]anthracene	3.91	2.19	2.6 ± 0.3
triphenylene	1.09	0.89	
chrysene	5.10	3.39	
benzo[b+j]fluoranthene	8.82	7.34	
benzo[k]fluoranthene	2.89	2.19	
benzo[a]fluoranthene	0.53		
benzo[e]pyrene	5.16	3.09	
benzo[a]pyrene	4.78	2.90	2.9 ± 0.5
perylene	1.21	1.24	
indeno[1,2,3-cd]pyrene	3.60	3.39	3.3 ± 0.5
benzo[ghi]perylene	4.78	4.61	4.5 ± 1.1
^a 5 minutes ultrasonic extraction with dicloromethane (5.042 mg), uncertainties estimated at $\pm 10\%$. ^b 16 hour soxhlet extraction with dichloromethane (17.844 mg), uncertainties estimated at $\pm 10\%$. ^c Certified concentrations.			

Table 8. PAH Contamination (ng) in XAD Laboratory and Field Blanks^a

PAH	XAD Laboratory Blank	XAD Field Blank
naphthalene	2.1	9.5
2-methylnaphthalene	0.3	1.0
1-methylnaphthalene	0.3	0.8
biphenyl	< 0.3	1.0
phenanthrene	1.8	1.0
benzo[e]pyrene	1.8	2.7
benzo[a]pyrene	1.6	0.8
^a Estimated detection limits for PAHs not observed in the XAD blank extracts is 0.3 ng.		

Table 9. Concentrations of PAHs Measured in XAD Samples (ng/m³)^a

PAH	XAD-01 Upstream Segment ^b	XAD-01 Downstream Segment ^c	XAD-05 Upstream Segment ^d	XAD-05 Downstream Segment ^e
naphthalene	95.8	≤ 36.5	28.2	≤ 16.3
1-methylnaphthalene	22.7	≤ 3.8	10.6	≤ 1.7
2-methylnaphthalene	12.7	≤ 3.1	6.2	≤ 1.4
biphenyl	8.1	≤ 1.5	7.4	≤ 0.7
acenaphthylene	44.6	1.9	45.5	1.7
acenaphthene	6.9	1.1	6.5	0.5
fluorene	13.9	3.5	9.4	1.9
dibenzothiophene	2.7	1.9	1.9	0.9
phenanthrene	≤ 7.3	≤ 7.3	7.2	≤ 3.3

^a Results were blank corrected (see Table 8). Results reported as ≤ x are indistinguishable from field blank levels.

^b Upstream XAD segment collected at Royal Saudi Naval Base.

^c Downstream XAD segment collected at Royal Saudi Naval Base.

^d Upstream XAD segment collected at King Fahad Military Medical Center.

^e Downstream XAD segment collected at King Fahad Military Medical Center.

Table 10. Concentrations and Detection Limits of PAHs Measured in Teflon Filter Samples ^a

PAH	Teflon Filter Blank (ng)	Teflon Filter PAH-01 (RSNB) ^b		Teflon Filter PAH-05 (KFMMC) ^c	
		(ng)	(ng/m ³)	(ng)	(ng/m ³)
naphthalene	0.4	≤ 0.1	≤ 1.5	0.5	0.9
2-methylnaphthalene	0.1	0.2	0.8	0.2	0.3
1-methylnaphthalene	0.4	≤ 0.1	≤ 0.4	≤ 0.1	≤ 0.2
biphenyl	0.1	≤ 0.1	≤ 0.4	≤ 0.4	≤ 0.2
acenaphthylene	0.1	≤ 0.1	≤ 0.4	≤ 0.1	≤ 0.2
acenaphthene	< 0.2	< 0.2	< 0.6	< 0.2	< 0.3
fluorene	< 0.1	< 0.4	< 0.4	< 0.1	< 0.2
dibenzothiophene	< 0.8	< 0.8	< 3.1	< 0.8	< 1.4
phenanthrene	3.4	≤ 3.4	≤ 13.1	≤ 3.4	≤ 5.8
anthracene	< 0.7	< 0.7	< 2.7	< 0.4	< 1.2
4,5-methylenephenanthrene	< 0.8	< 0.8	< 3.1	< 0.8	< 1.4
3-methylphenanthrene	< 0.6	< 0.8	< 3.1	< 0.8	< 1.4
2-methylphenanthrene	< 0.8	< 0.8	< 3.1	< 0.8	< 1.4
4- and 9-methylphenanthrene	< 0.8	< 0.8	< 3.1	< 0.8	< 1.4
1-methylphenanthrene	< 0.8	< 0.8	< 3.1	< 0.8	< 1.4
fluoranthrene	< 0.6	0.7	2.7	0.6	1.0
acephenanthrylene	< 0.6	< 0.6	< 2.3	< 0.8	< 1.0
pyrene	< 0.5	0.6	2.3	< 0.5	< 0.9
benz[a]anthracene	< 0.6	< 0.6	< 2.3	< 0.6	< 1.0
triphenylene	< 0.8	< 0.6	< 2.3	< 0.6	< 1.0
chrysene	< 0.6	< 0.6	< 2.3	< 0.6	< 1.0
benzo[b+j]fluoranthene	< 0.4	< 0.4	< 1.5	< 0.4	< 0.7
benzo[k]fluoranthene	< 0.4	< 0.4	< 1.5	< 0.4	< 0.7
benzo[a]fluoranthene	< 0.4	< 0.4	< 1.5	< 0.4	< 0.7
benzo[e]pyrene	2.4	4.1	15.8	≤ 2.4	≤ 4.1
benzo[a]pyrene	< 0.4	< 0.4	< 1.5	< 0.4	< 0.7
perylene	< 0.4	< 0.4	< 1.5	< 0.4	< 0.7
indeno[1,2,3-cd]pyrene	< 0.3	< 0.3	< 1.1	< 0.3	< 0.5
benzo[ghi]perylene	< 0.3	< 0.3	< 0.1	< 0.3	< 0.5

^a "< x" refers to species not detected in blank or samples. "≤ x" refers to sample concentrations indistinguishable from blank contamination levels.

^b RSNB - Royal Saudi Naval Base, Al-Jubail.

^c KFMMC - King Fahad Military Medical Center, Dhahran.

Table 11. Concentrations and Detection Limits of PAHs Measured in PM10 Filter Samples ^a

PAH	PM10 Blank (ng)	PM10-01 (KFMMC) ^b		PM10-02 (KFMMC) ^c		PM10-03 (RSNB) ^d	
		(ng)	(ng/m ³)	(ng)	(ng/m ³)	(ng)	(ng/m ³)
naphthalene	27.3	52.4	37.1	53.6	44.7	29.6	< 60
2-methylnaphthalene	< 10.0	< 10.0	< 14.8	< 10.0	< 17.0	< 14.3	< 22.2
1-methylnaphthalene	< 10.0	< 10.0	< 14.8	< 10.0	< 17.0	< 14.3	< 22.2
biphenyl	< 10.0	< 10.0	< 14.8	< 10.0	< 17.0	< 10.0	< 22.2
acenaphthylene	< 10.0	< 10.0	< 14.8	< 10.0	< 17.0	< 14.3	< 22.2
acenaphthene	< 10.0	< 10.0	< 14.8	< 10.0	< 17.0	< 14.3	< 22.2
fluorene	< 10.0	< 10.0	< 14.8	< 10.0	< 17.0	< 14.3	< 22.2
dibenzothiophene	< 5	18.5	27.4	32.0	54.4	< 5	< 11.1
phenanthrene	43.7	89.2	67.5	77.4	57.5	< 43.7	< 97
anthracene	< 5	10.0	10.0	28.8	49.0	< 5	< 11.1
4,5-methylenepheneanthrene	< 5	< 5	< 7.4	< 5	< 8.5	< 5	< 11.1
3-methylphenanthrene	< 5	24.5	36.3	17.6	29.9	< 5	< 11.1
2-methylphenanthrene	< 5	28.6	42.4	21.6	37.2	52.9	117
1-methylphenanthrene	< 5	23.3	34.6	62.3	106	53.9	110
fluoranthrene	16.4	103	128	88.7	123	51.8	78.3
acephenanthrylene	< 5	25.5	37.8	21.6	36.7	10.0	22.2
pyrene	12.0	116	154	103	155	53.2	91.3
benz[a]anthracene	3.4	111	163	137	226	35.9	72.1
triphenylene	1.8	not resolved ^e		not resolved ^e		20.8	42.1
chrysene	5.5	246	354	349	582	59.5	120
benzo[b+j]fluoranthene	< 5	467	693	536	911	129	286
benzo[k]fluoranthene	10.6	103	195	158	250	33.1	49.9
benzo[a]fluoranthene	< 5	48.9	72.5	59.2	101	12.1	26.8
benzo[e]pyrene	2.9	245	359	289	486	72.1	153
benzo[a]pyrene	3.6	227	332	301	505	53.3	110
perylene	< 5	30.2	44.8	42.7	72.6	9.5	21.1
indeno[1,2,3-cd]pyrene	5.2	316	460	373	624	91.6	192
benzo[ghi]perylene	5.4	554	814	653	1102	168	361

^a Airborne concentrations (pg/m³) are corrected for filter blank contamination.

^b KFMMC - King Fahad Military Medical Center, Dhahran, roof of hospital.

^c KFMMC - King Fahad Military Medical Center, Dhahran, roof of apartment building.

^d RSNB - Royal Saudi Naval Base, Al-Jubail, roof of hospital.

^e Triphenylene not resolved from chrysene. Chrysene results represent sum of triphenylene and chrysene concentrations.

Results for three PM-10 filter samples and a filter blank are shown in Table 11. Though it would be expected to exist mainly in the vapor phase under the conditions of sampling, naphthalene was detected above filter blank concentrations in two of the three filter samples (PM-10-01 and PM-10-02, collected at two sites at KFMMC). The PM-10-01 and PM-10-02 had comparable levels of PAHs, with filter PM-10-02 having somewhat higher concentrations of the higher molecular weight species (benzo[b+j]fluoranthene through benzo[ghi]perylene). Although PM-10-03 was collected near the heavily-industrialized coastal city of Al-Jubail, airborne PAH concentrations for this sample were typically 2 to 4 times lower than those measured in samples PM-10-01 and PM-10-02, collected at the King Fahad Military Medical Center, near Dhahran. Atmospheric concentrations of PAHs and other species (e.g., trace elements) vary over orders of magnitude depending on source emissions (local and regional) and meteorology. The fact that we observed higher PAH concentrations at what was thought to be a background site (KFMMC), suggests that perhaps a local source (i.e., the hospital incinerator) and/or the meteorology (vertical mixing height) influenced the collected samples. Only after collecting and analyzing a larger number of samples, as during a monitoring program, would we have a better feel for which site routinely had higher airborne PAH concentrations. Comparing the three samples collected in Saudi Arabia with those collected as part of studies in the United States, geometric mean PAH concentrations for 36 samples collected in Boise, Idaho (U.S.A) were at least a factor of ten higher than the three collected in the Kingdom. Samples collected in Roanoke, Virginia (U.S.A) as part of a study similar to that of Boise yielded PAH concentrations of the same order of magnitude as the Saudi samples. These comparisons are limited by the small number of Saudi samples. We feel that the value of a long-term monitoring program in Saudi Arabia is evident by the data discussed in this report. A program involving the collection and analysis of air samples (e.g., PM-10 Hi-Vol) in a Saudi Arabian city (e.g., Riyadh, Al-Jubail, Dhahran) would provide valuable data for determining current airborne PAH concentrations as well as for devising air pollution control strategies for the future.

4.2 Laser Microprobe Mass Spectrometry

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4.2.1 Introduction

The laser microprobe mass spectrometer (LMMS) is a time-of-flight mass spectrometer that utilizes a high powered laser to vaporize and ionize the sample material. The sample is viewed optically and a particle is selected for analysis by aiming a co-aligned pilot helium-neon (HeNe) laser beam spot onto the particle. The ionizing laser is a high power, pulsed Nd:YAG laser frequency quadrupled to provide UV radiation (266 nm). The radiation is focused onto the sample by a quartz optical microscope objective. The high power pulse, 10 nanoseconds in duration, evaporates the sample and in the process ionizing some of the atoms. All ions generated are accelerated to uniform translational energy and mass-separated by time-of-flight mass spectrometry. In time-of-flight mass

spectrometry, flight time in the drift tube is proportional to the square root of the mass-to-charge ratio. The arrival of the ion packets at the end of the drift tube is determined by a secondary ion/electron multiplier detector.

The instrument used, the LAMMA 500, has transmission geometry which refers to having the laser beam and the mass spectrometer in-line. A complete description of LMMS is given by Denoyer et al. [14], Hercules et al. [15] and Simons [16]. Single particle analysis is discussed by Kaufmann [17], by De Waele and Adams [18] and by Wieser and Wurster [19]. Early work in aerosol research applications is presented by Wieser, Wurster and Seiler [20].

Some of the important aspects of the LMMS instruments are nominal micrometer spatial resolution, high detection sensitivity and detection capability for either positive and negative ions produced in the laser ionization. In addition, it is usually possible to determine the elemental, isotopic and in many cases even the molecular composition of a particle. LMMS is generally not considered quantitative even for major constituents, except with regard to isotope abundance. Matrix effects in the sample play a dominant role during the laser beam-sample interaction, making quantitation difficult. The main strength of LMMS lies in providing useful qualitative information.

4.2.2 Sample Preparation and Analysis

The samples analyzed by LMMS came from the Mylar and stainless steel impactor substrates and a quartz fiber filter. Particles collected on Mylar from stage 8, 7, 6 and 5 (MA-02-8, MA-2-7, MA-2-6 and MA-2-5) that correspond to particle cut sizes of 0.6, 1, 2 and 3.5 μm were transferred to Formvar [a poly(vinyl formal)resin] coated copper transmission electron grids and mounted into the LAMMA 500 without further preparation. Particles from these stages and from MA-01-8 (stainless steel substrate) were also mounted on the back side of the quartz coverslip to analyze primarily for carbon. Quartz fibers containing attached particles taken from the PM-10-01 filter were mounted across an uncoated copper TEM grid and individual particles were ablated from the fibers. This fiber filter collects all particles less than 10 μm . Quartz fiber filters are especially efficient for small, submicrometer particles due to the large surface area and the relatively high diffusion coefficient of small particles.

Both single and multiple particles were ablated with the laser and mass analyzed. By ablating more than one particle, sensitivity for trace elements and compounds is enhanced. The samples mounted on the quartz coverslip were analyzed using a large, defocused laser beam that ionizes material from particles on the coverslip in a 50 to 100 μm diameter spot. The defocus mode allows detection of molecular species, especially organic compounds that may be present in the sample. Both positive and negative ion spectra were taken. Over 200 spectra were collected at both the highest sensitivity available to the instrument and at a factor of ten lower sensitivity.

4.2.3 Results and Discussion

The results of analysis by LMMS indicate that the samples are primarily inorganic fine dust particulate material. This is based on the fact that for all the samples analyzed, the characteristic carbon cluster pattern was not found in abundance. However, some of the samples did show carbon to be present in small amounts as evidenced by the sequence of m/z peaks at 12, 24, 36,...72. No organic molecular species were detected in the samples. An optical micrograph in transmitted light is presented in Figure 1 of MA-02-8 mounted on a quartz coverslip. The particles appear, for the most part, to be less than 1 μm and somewhat rounded in shape.

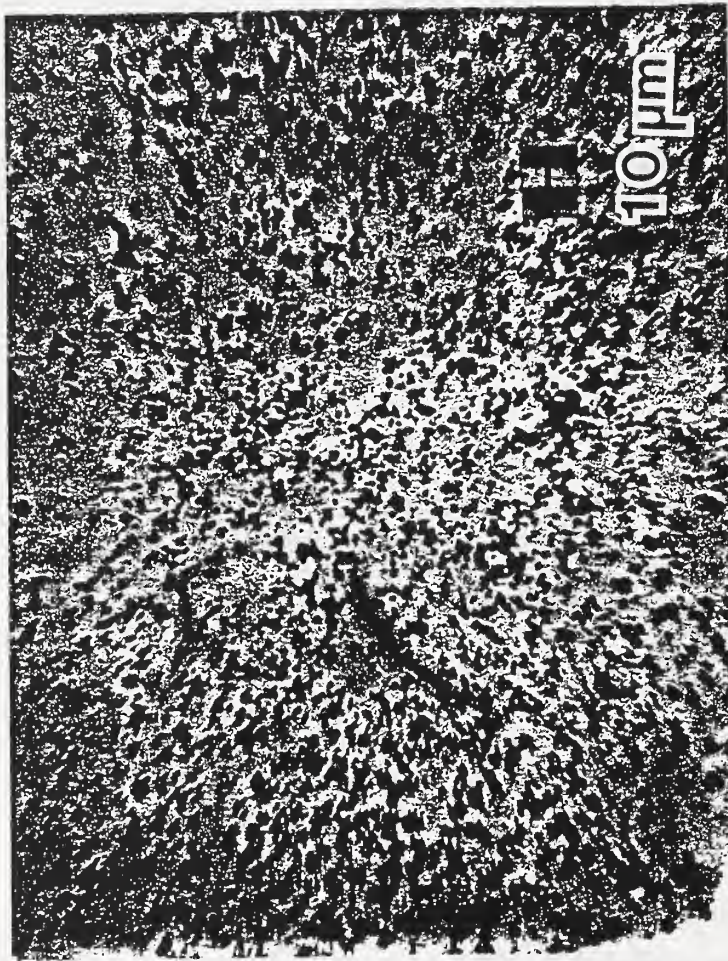


Figure 1. Optical micrograph of fine particulate material taken from stage MA-02-8 viewed in transmitted light.

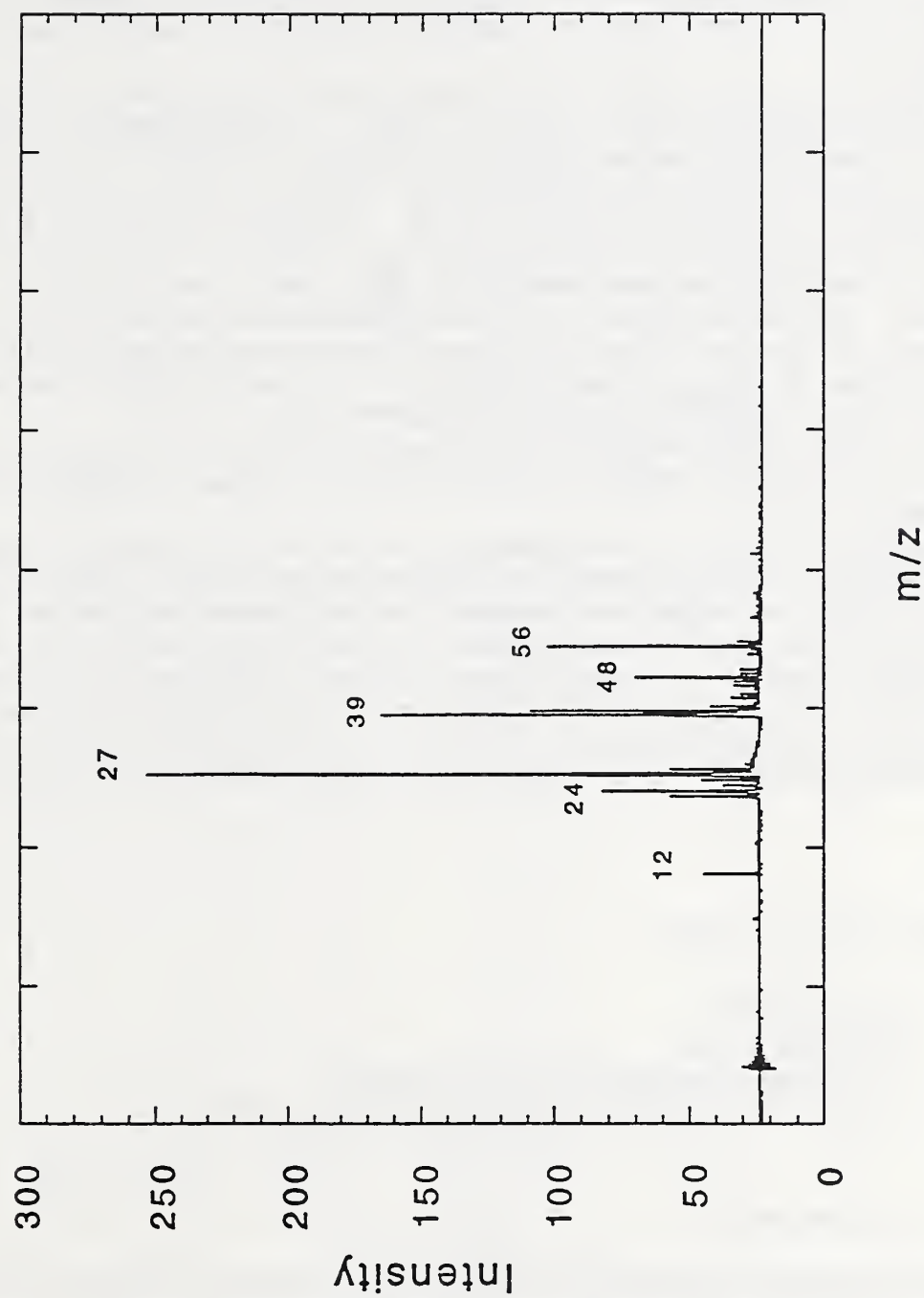


Figure 2. Positive ion mass spectrum that results from averaging 9 spectra of particulate material from stage MA-02-8.

A positive ion spectrum is presented in Figure 2 that is composed of the average of 9 spectra from MA-02-8. The positive ions identified in various spectra taken of MA-02-8 material are presented in Table 12.

Evidence for these identifications is based on peak patterns resulting from isotopic abundances and from the cluster ions that form from the major constituents. Figure 3 shows an expanded scale of the average spectrum shown in Figure 2. A typical negative ion spectrum of MA-01-8 particulate material is shown in Figure 4. The negative ions observed and their identification is found in Table 6.

Samples MA-02-7, MA-02-6, and MA-02-5 produced mass spectra similar to MA-02-8. A positive ion average spectrum for MA-02-7 is shown in Figure 5. Peak identification is similar to MA-02-8. A typical negative ion mass spectrum is shown in Figure 6 for MA-02-7 which is likewise similar to the respective spectra found for MA-02-8 material. Particles attached to quartz fibers from the filter mentioned above indicated the presence of Pb. A positive ion average (of 8 spectra) spectrum of particles attached to the quartz fibers is presented in Figure 7. An expanded low sensitivity single particle mass spectrum is shown in Figures 8 and 9. Note the isotopes of Pb are clearly shown in Figure 9. Lead was not found on any of the impactor surfaces analyzed, but was readily found on the fibers. It is thought that the Pb particles are $<0.1\text{ }\mu\text{m}$ in size and thus are not collected on the impaction stages. However, since the fiber filter serves as an excellent collection material for small particles, the small particles containing Pb were collected there.

Particulate material from MA-01-8, the lowest impactor stage with stainless steel substrates, was transferred to a cleaned quartz coverslip for LMMS analyzing for carbon. Negligible carbon was found in the positive ion mode.

In summary, the particulate matter collected on the bottom four stages of the impactor sampler were analyzed by LMMS and found to be primarily inorganic fine dust. Minimum sample preparation was required, the particles were transferred from the impactor substrate onto either a formvar coated grid surface or onto a quartz coverslip. Over 200 mass spectra were taken in both positive and negative ion mode. This material appears to be fine particle matter that is composed of Na, Mg, Al, Si, K, Ca, Fe, Ti, and some Ba. Particles collected by PM-10-01 quartz fibers were analyzed by ablating the particles directly from the fibers. The particles found on the quartz fiber filter contained lead. There appears to be very little carbon molecular species present in the samples analyzed.

4.3 Micro-Raman Analysis

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4.3.1 Introduction

Micro-Raman analysis was performed on several air particulate samples collected by a cascade impactor sampler. The particulate material collected on two of the impactor stages, i.e., stages MA-01-6 (cut-off diameter $2.0\text{ }\mu\text{m}$) and MA-01-8 (cut-off diameter $0.6\text{ }\mu\text{m}$), was examined in the Raman

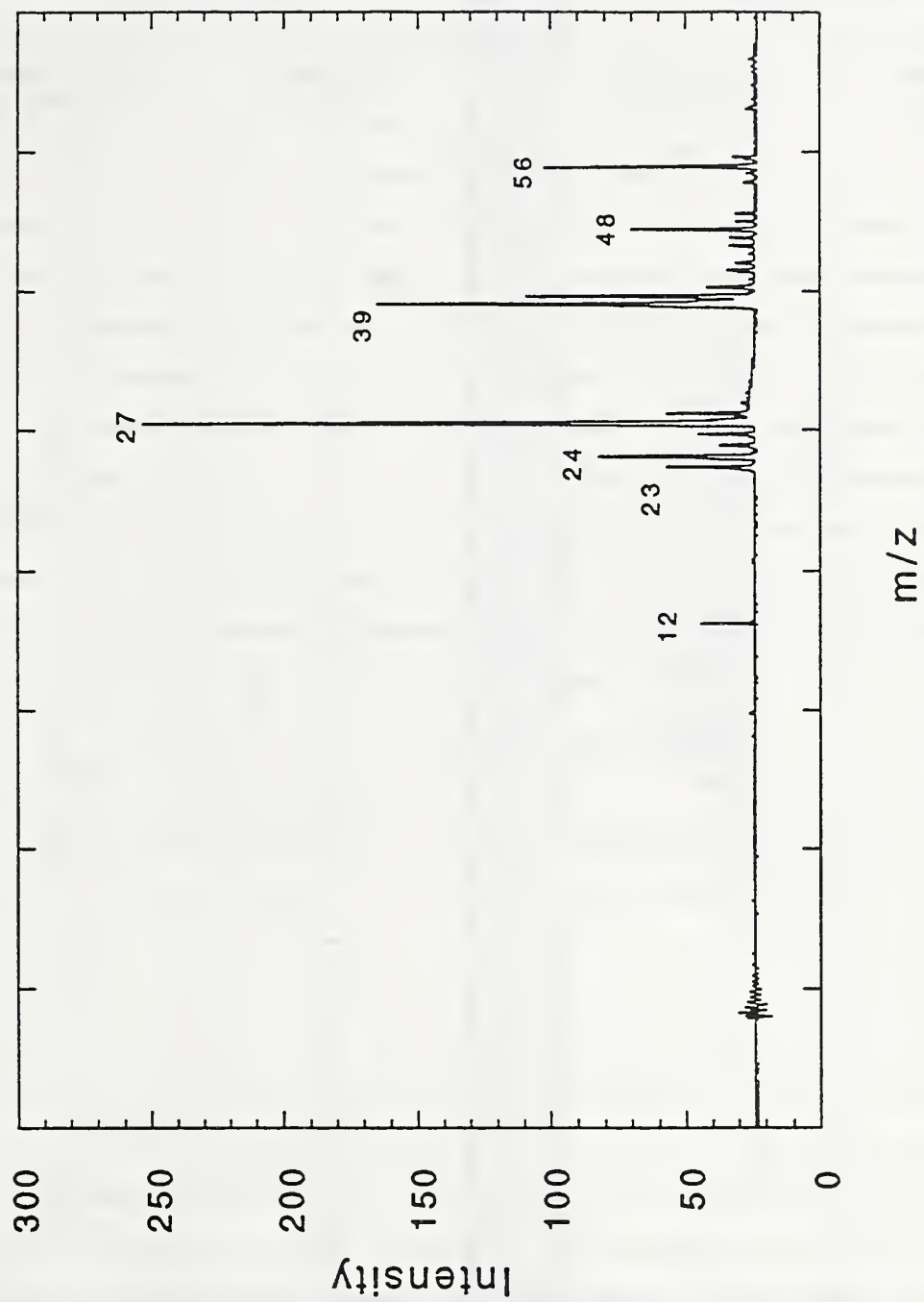


Figure 3. Expanded version of spectrum shown in Figure 2.

Table 12. Particles Analyzed from Mylar Substrate of Marple Cascade Impactor

Possible Identification of Particles from Sample MA-02-108		Possible Identification of Particles from Sample MA-02-107	
Mass/Charge (m/z)	Possible Positive Ion Species	Mass/Charge (m/z)	Possible Negative Ion Species
6	Li	1	H
7	Li	12	C
12	C	13	CH
23	Na	16	O
24	Mg, C ₂	17	OH
27	Al	24	C ₂
28	Si	25	C ₂ H
39	K	26	CN, C ₂ H ₂
40	Ca	31	P
48	Ti	35, 37	Cl
56	Fe, CaO	36	C ₃
57	CaOH	42	CNO
138	Ba	59	AlO ₂
		60	SiO ₂ , C ₃
		69	?
		72	C ₆ , FeO
		76	SiO ₃
		84	C ₇
		97	?
		103	?
		119	AlSiO ₄
		179	AlSi ₂ O ₆

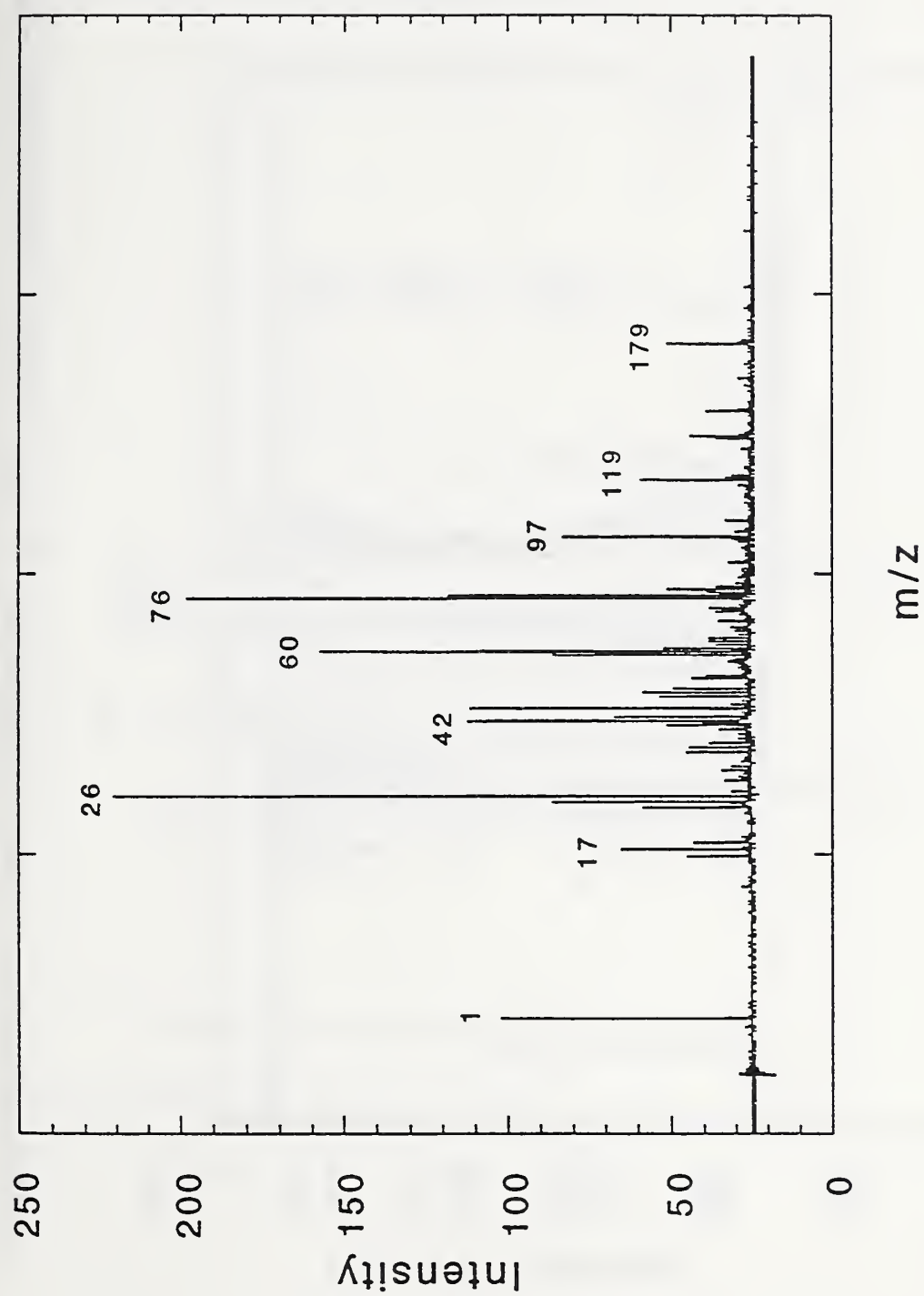


Figure 4. Single typical negative ion mass spectrum of MA-02-8 material.

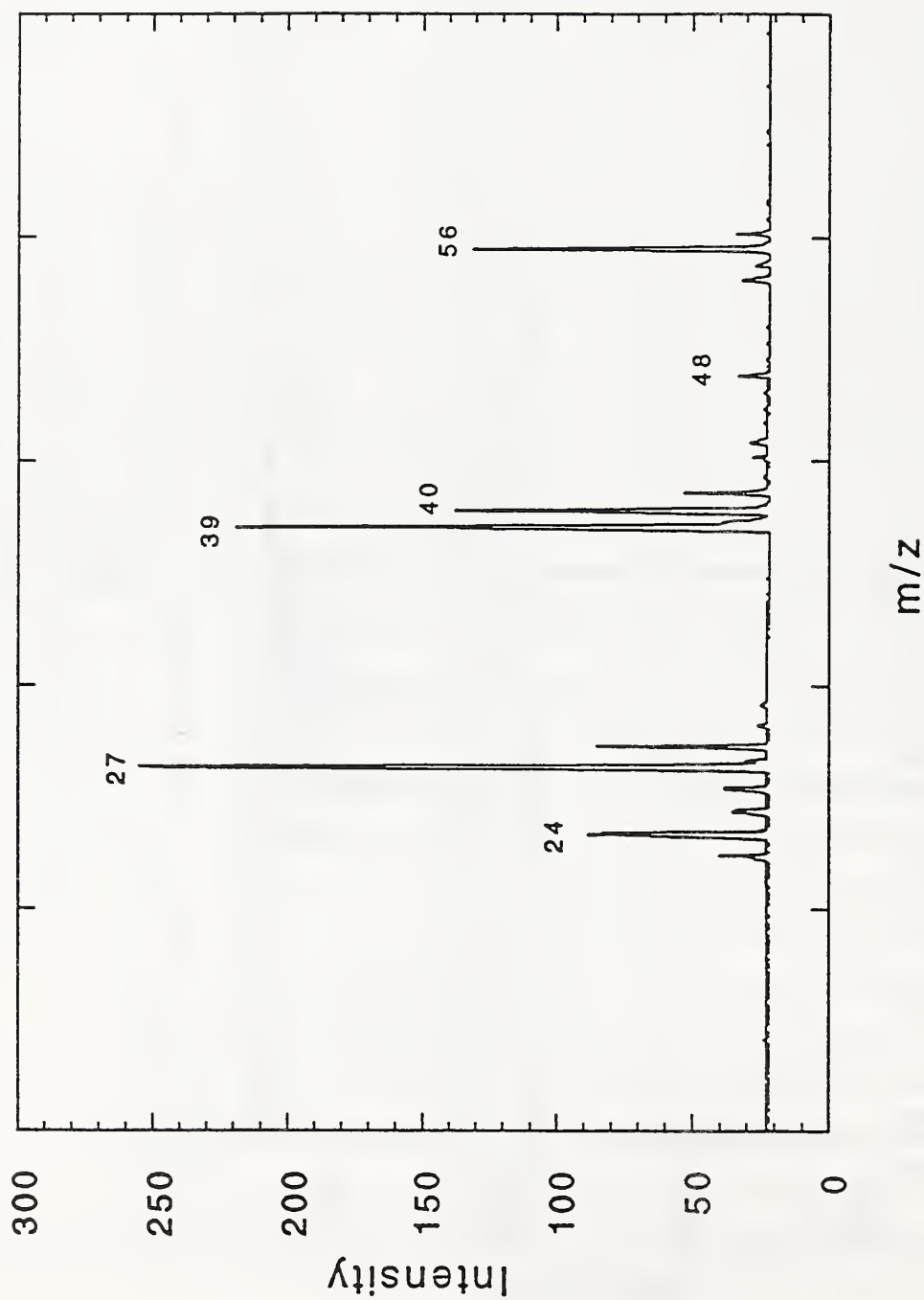


Figure 5. Expanded section of a positive ion spectrum that is the average of 8 spectra of MA-02-7 particle matter.

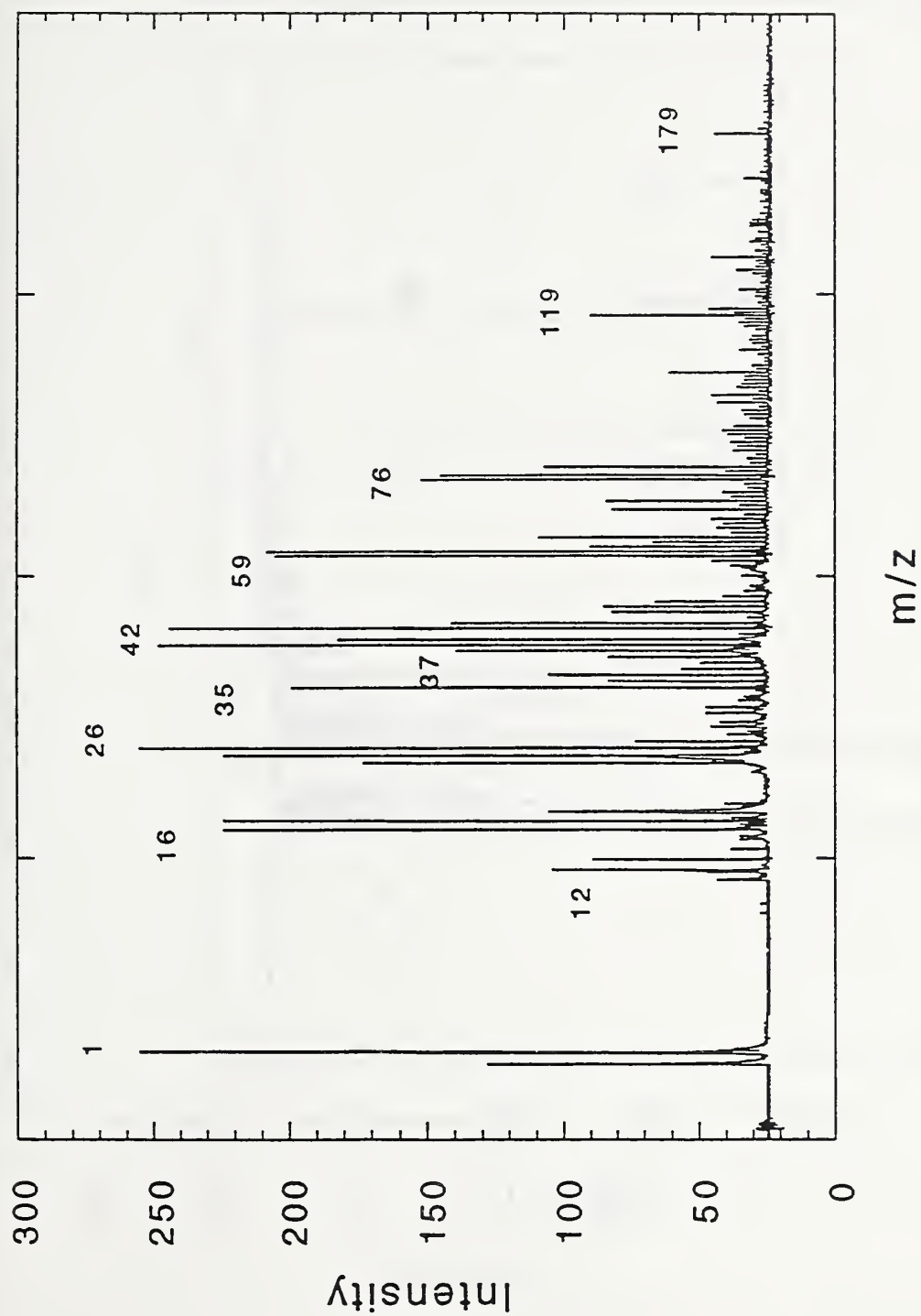


Figure 6. Single typical negative ion mass spectrum of MA-02-7 material.

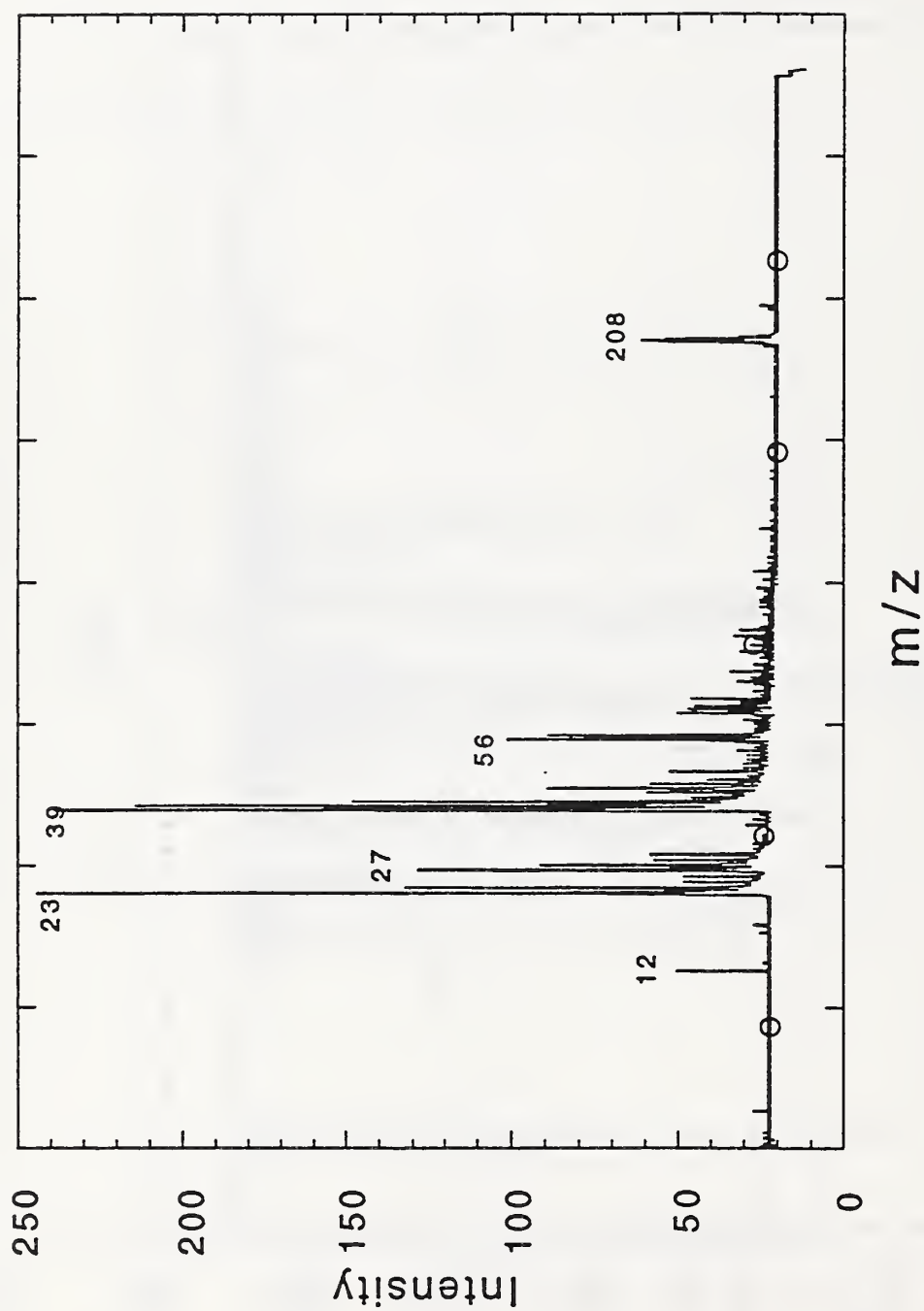


Figure 7. Positive ion mass spectrum that results from averaging 8 spectra produced from particles attached to quartz fiber filter material.

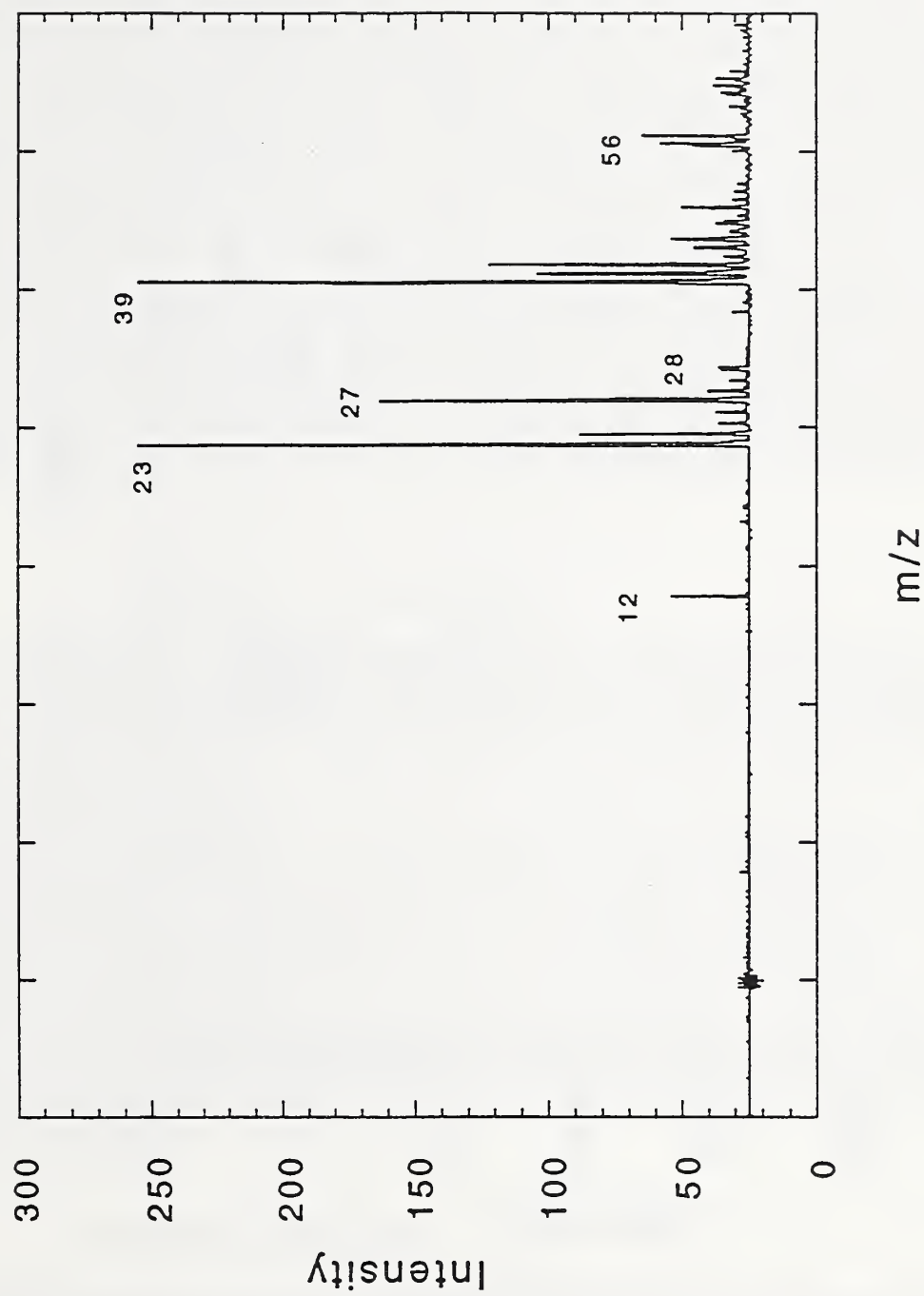


Figure 8. Single positive ion mass spectrum of a particle attached to the quartz fiber illustrating the isotopic pattern found for lead.

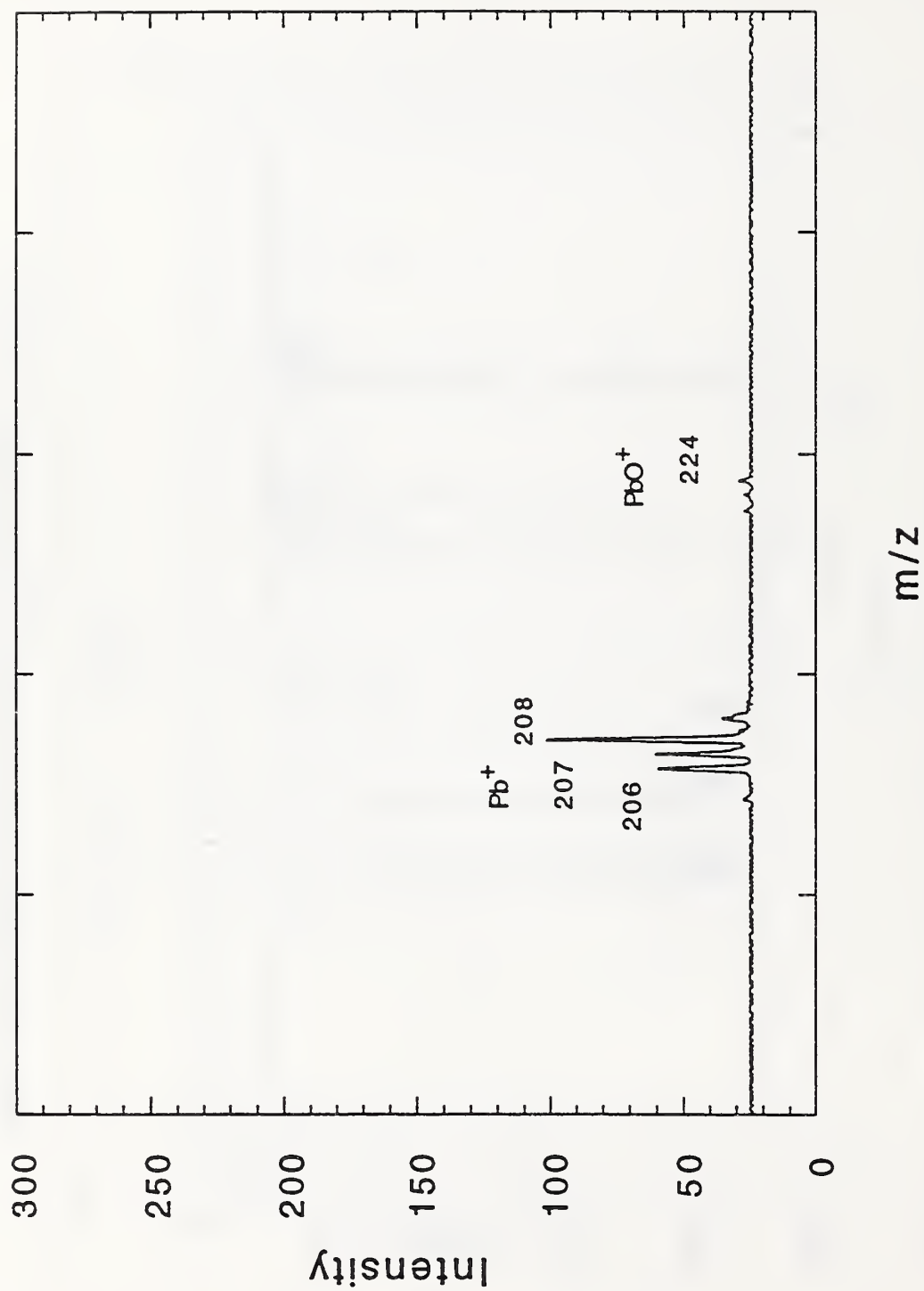


Figure 9. Single positive ion mass spectrum of a particle in Figure 8 shown with expanded scale illustrating the isotopic pattern found for lead.

microprobe with the aim of obtaining molecular, or compound, information on the collected material.

Raman spectroscopy furnishes a vibrational spectrum indicative of chemical bonding and of crystallographic structure, in the case of molecular solids. In the absence of any interfering fluorescence or luminescence from the sample, the Raman spectrum of most compounds generally serves as a diagnostic "fingerprint", much like the closely related infrared spectrum. Present-day Raman microprobes, permitting probing the sample at the microscopic level, can acquire this analytical information with spatial information down to 1 μm and a detection limit of about 1 pg.

To illustrate the specificity of the Raman spectrum for common natural minerals, the microprobe spectra of natural calcite (CaCO_3) and natural quartz ($\alpha\text{-SiO}_2$) are shown in Figures 10 and 11. As molecular solids become more complex, in terms of the variety of chemical bonds that are Raman active, the complexity of the vibrational spectrum increases, manifesting itself in a multitude of characteristic vibrational bands, indicative of functional group vibrations. This is illustrated in Figure 12 with the spectrum of the organic explosive HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane) showing numerous bands over the Raman frequency range plotted out. The Raman microprobe spectra of the two common minerals referred to here (Figure 10 and 11) and that of the organic nitro-compound (Figure 12) each exhibit good signal-to-background relationships, whereby the expected (and observed) Raman bands are unobscured by a possibly moderate or high spectral background that sometimes arises from sample fluorescence or luminescence. The source of any sample fluorescence or luminescence may often be sample impurities, such as trace contaminants, or may stem from the sample itself. Polynuclear aromatic hydrocarbons (PAHs) tend to be intrinsically highly fluorescent (due to their electronic structure) in Raman measurements with visible laser excitation.

4.3.2 Sample Preparation and Analysis

To examine the particulate material collected by the size-segregating impactor sampler, we employed a commercial Raman microprobe. This instrument is of the dispersive design, employing an optical multichannel detector (SIT-diode array), and using the monochromatic emission lines from either an Argon-ion laser (e.g., 514.5 nm, 488.0 nm), or a Krypton-ion laser (e.g., 647.1 nm) as excitation sources.

We obtained the Raman spectra of these samples with both 514.5 nm (green) and 647.1 nm (red) excitation to examine the fluorescence behavior of these samples at these two different excitation frequencies. In general, any sample fluorescence observed with 514.5 nm excitation is usually less pronounced, and often totally absent, when the spectra are excited at 647.1 nm.

With the focused laser spot (beam spot of $\approx 2 \mu\text{m}$ diameter) of the Raman microprobe we could examine the impacted particulate material for homogeneity of composition, to discern any differences in composition, if present. The particulate material collected on the stainless-steel foils of stages MA-01-6 and MA-01-8 of the impactor consists of extensively aggregated, piled-up, finely-sized dust of uniform appearance and morphology. Microscopic aggregates of this material in various parts of these two collection surfaces were examined in the Raman microprobe by entirely routine measurement procedures.

4.3.3 Results and Discussion

Every part of this collected fine dust, on both stages, gave rise to intense, diffuse yellow luminescence as the spectra were excited with 514.5 nm radiation. This luminescence did not

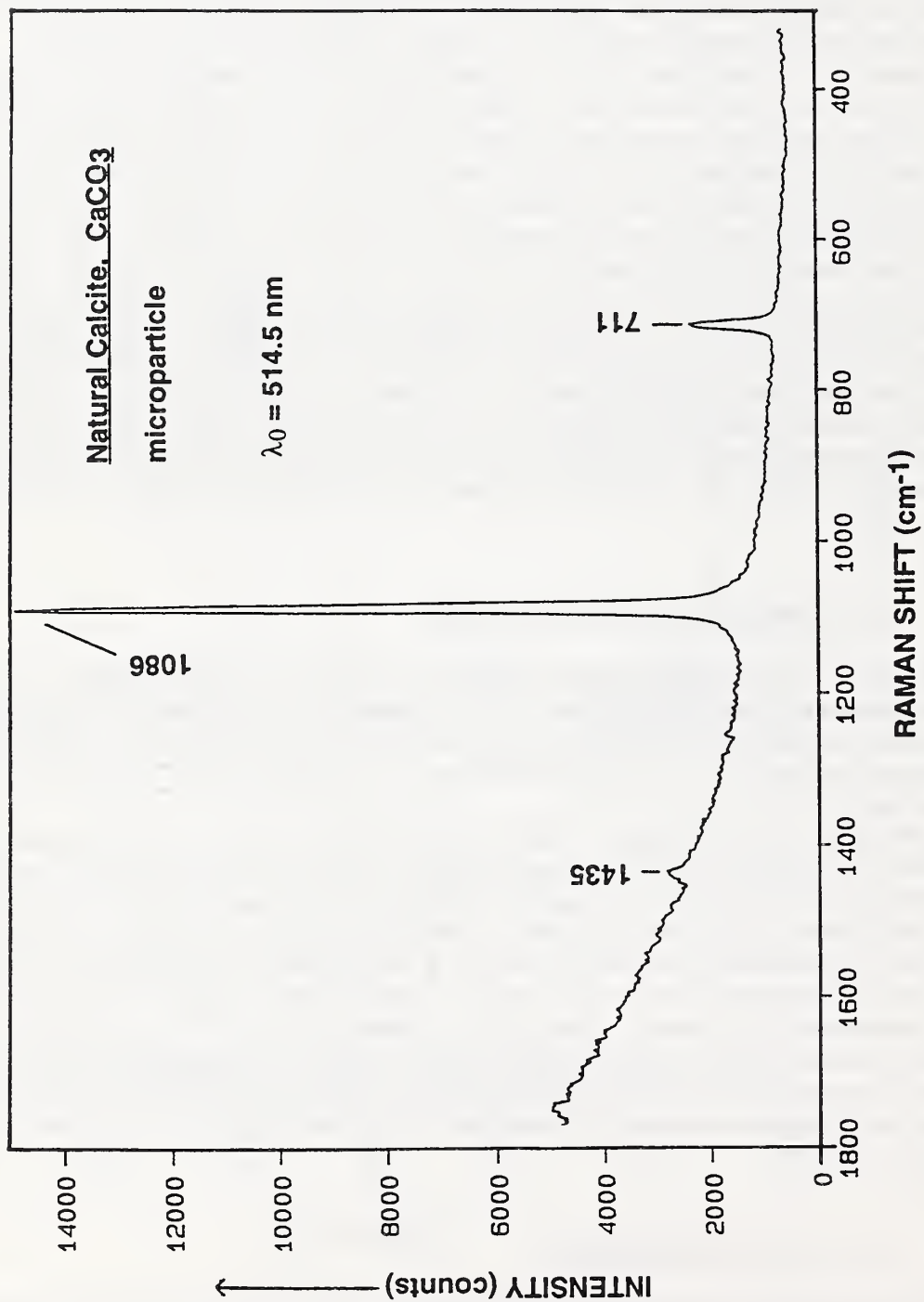


Figure 10. Raman microprobe spectrum of a single particle (size $\approx 8 \mu\text{m}$) of the mineral calcite, excited at 514.5 nm.

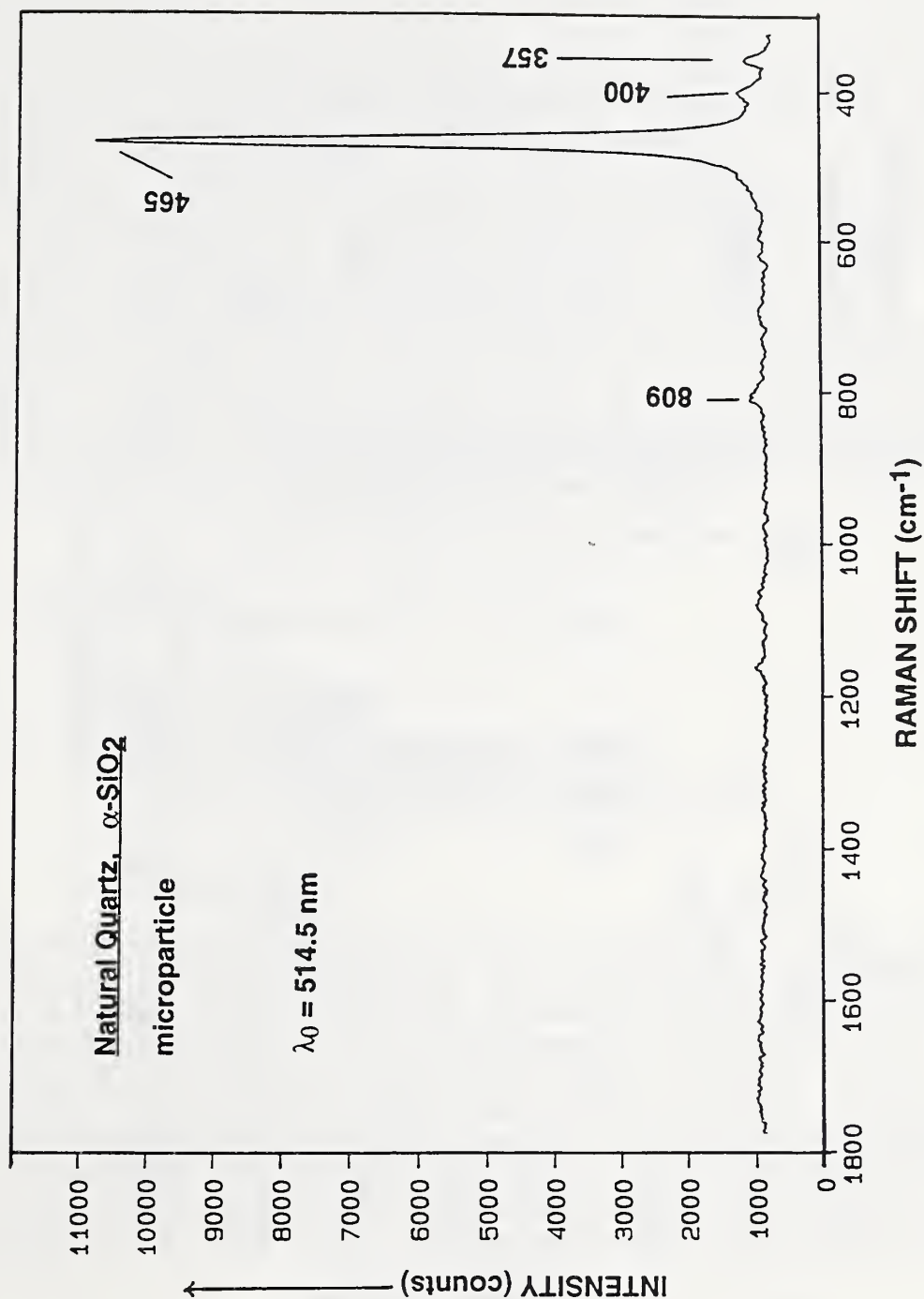


Figure 11. Raman microprobe spectrum of a particle (size $\approx 13 \mu\text{m}$) of natural quartz, excited at 514.5 nm.

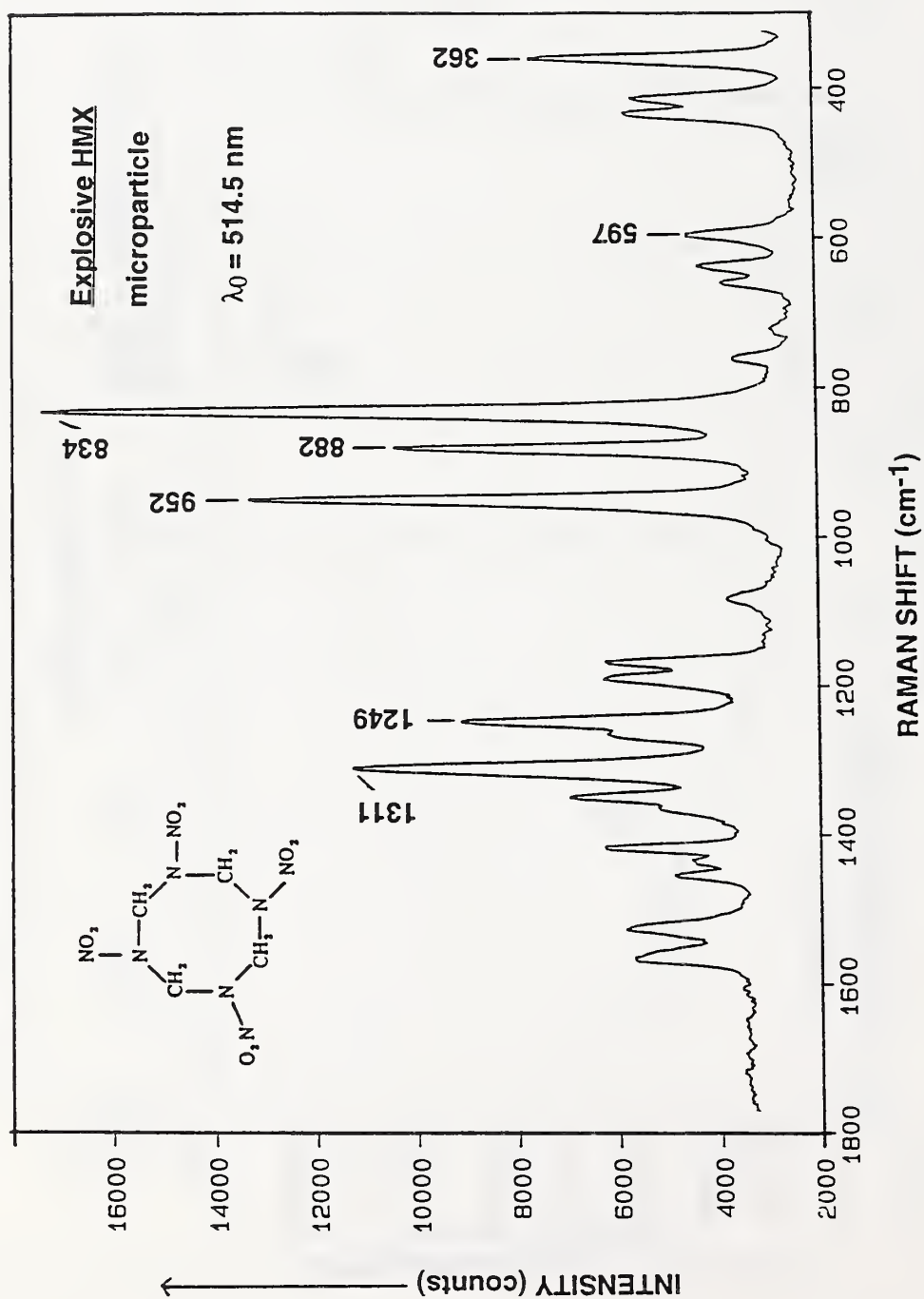


Figure 12. Micro-Raman spectrum of a microcrystal (size $\approx 10 \mu\text{m}$) of the high explosive HMX, excited at 514.5 nm.

sufficiently bleach away and diminish with time, upon prolonged irradiation, to permit informative spectra to be obtained.

Figures 13 and 14 show representative micro-Raman spectra of the particulate material collected on stages MA-01-6 and MA-01-8, excited at 514.5 nm. Both particulate fractions gave spectra showing broad-band fluorescence only, which in these cases masked any Raman features which may have been present in this spectral region. Common minerals, such as from earth's crustal material, invariably show Raman bands in the region from 300 to 1800 cm^{-1} , and so do most organic compounds and polymers.

When these same particulate fractions (on stages MA-01-6 and MA-01-8) were examined with 647.1 nm excitation (Figure 15), equally intense laser-excited luminescence was observed that prevented any Raman data to be obtained. Again, any potential Raman information was masked by these non-Raman emissions whose origin(s) are not known at this time.

We should point out that the spectra of the "reference" samples (Figures 10 to 12, of calcite, quartz, and HMX) were acquired in parallel with the impactor samples of this study, employing identical measurement conditions. Their spectra display the expected analytical information unobscured by a masking (fluorescent or luminescent) spectral background.

We speculate that a likely source of the observed luminescence from these air-particulate collections may be adsorbed, highly-fluorescing, organic material, or residue, present in sufficient concentrations, or even as a surface coating, to give rise to this overwhelming laser-excited luminescence. A careful removal of this presumed organic contamination, by either low-temperature ashing or solvent extraction, may clean up this particulate fraction enough to render this material in a form that will allow analytically useful Raman spectra to be obtained.

4.4 Environmental Scanning Electron Microscopy

Contributed by -

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4.4.1 Introduction

The Environmental Scanning Electron Microscope (ESEM) is appropriately suited to investigate particles (Wight and Zeissler [21]). The sample chamber in the ESEM operates at low vacuum [280-693 Pa (2.1-5.2 Torr)] and the gas molecules present are utilized to both drain surface charge and provide imaging gain. The neutralization of surface charge makes it possible to investigate insulating and particulate samples without applying a conductive coating. Use of the ESEM allows the sample to be later analyzed by other analytical techniques without the potential bias of conductive coatings and related preparation processes. The low vacuum of the sample chamber opens up electron microscopy to many samples (wet, volatile, loose particles, particles in oil, and loose fibers to name a few) that may not have been compatible with the high vacuum of conventional electron microscopy. A thorough review of the theory and operation of the ESEM can be found in Danilatos [14].

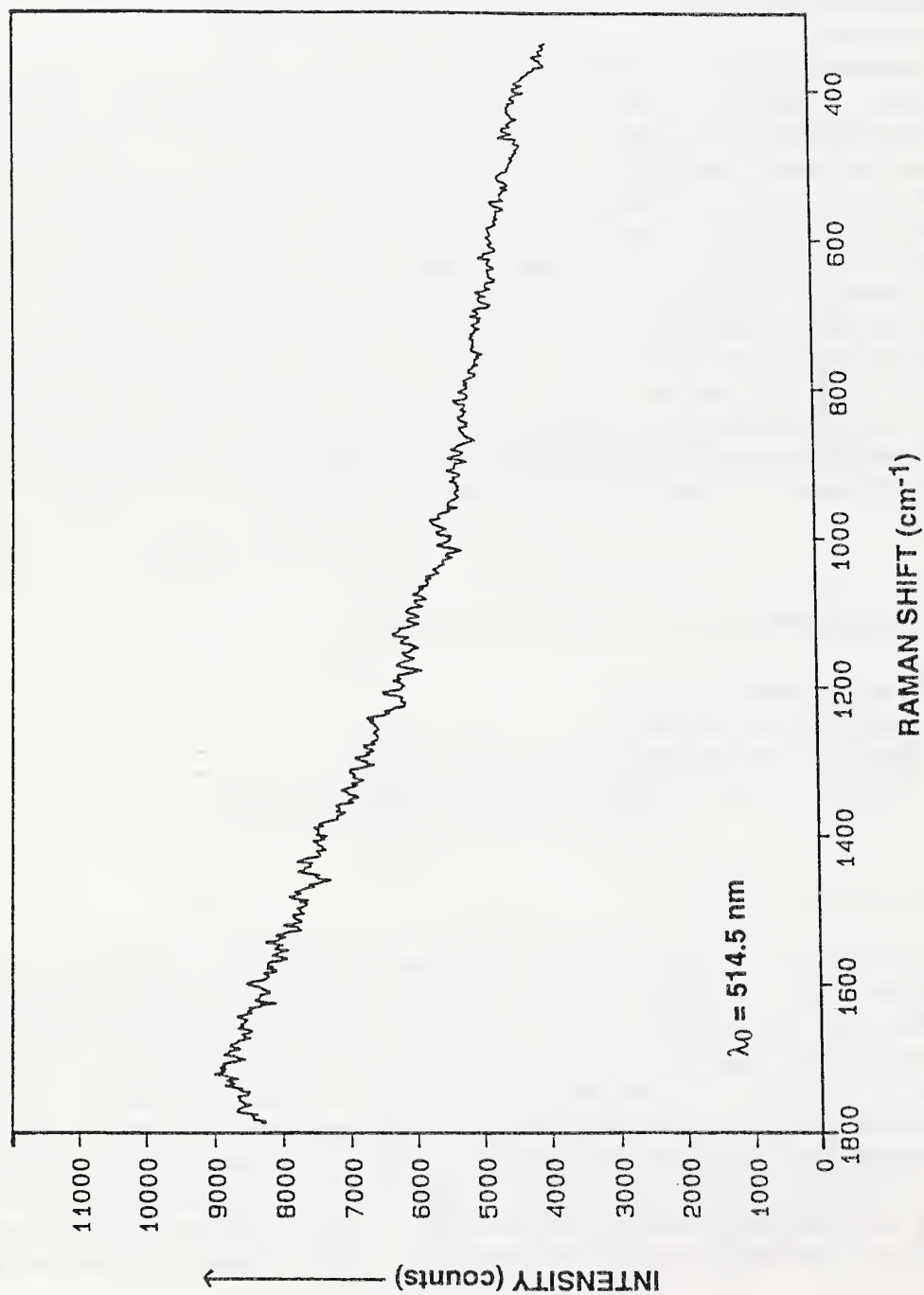


Figure 13. Representative micro-Raman spectrum of a particle agglomerate typical of the material collected on Stage MA-01-6. Analyzed on the stainless-steel substrate, with 514.5 nm excitation.

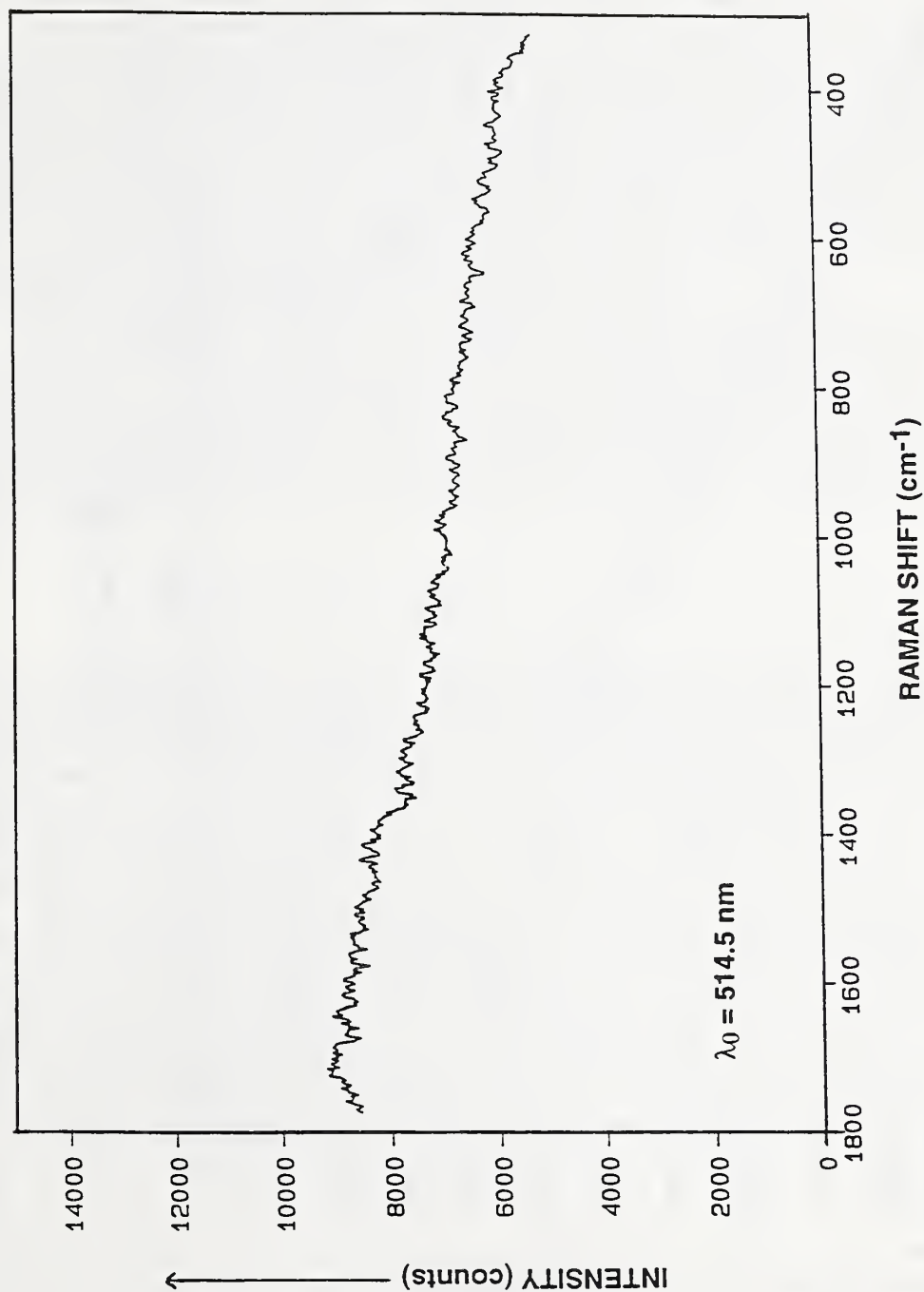


Figure 14. Representative micro-Raman spectrum of a particle agglomerate typical of the material collected on Stage MA-01-8. Analyzed on the stainless-steel substrate, with 514.5 nm excitation.

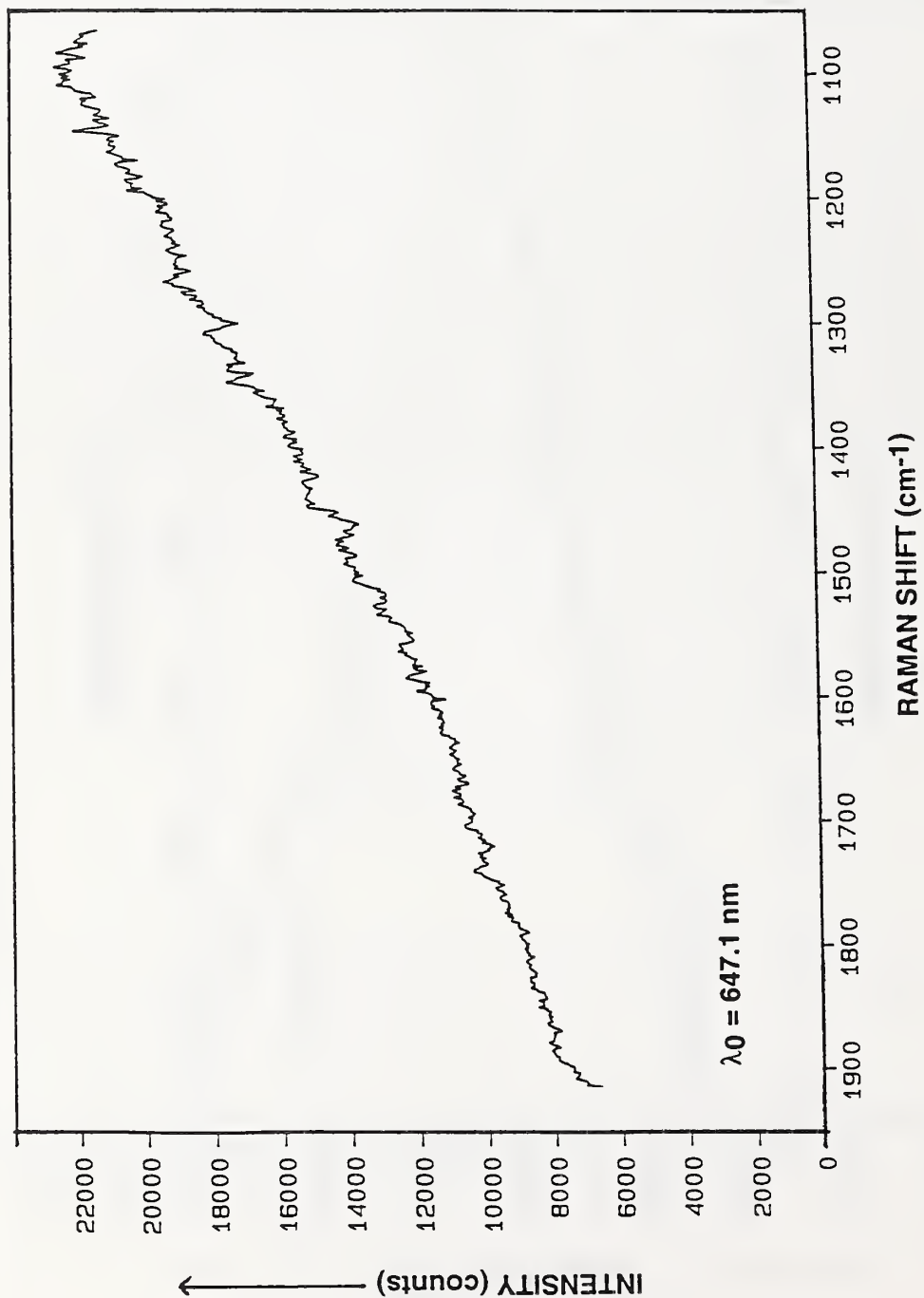


Figure 15. Representative micro-Raman spectrum of a typical particle agglomerate on Stage MA-01-6. Analyzed on the stainless-steel substrate, with 647.1 nm excitation.

4.4.2 Sample Preparation and Analysis

The samples were investigated in an Electroscan ESEM equipped with a gaseous detection device (Danilatos [15]) for secondary electron imaging and a scintillating backscatter detector. The instrument was equipped with a Noran Pioneer x-ray analysis system.

The samples consisted of XAD adsorbent, PM-10 filters, and impactor stages. XAD is an adsorbent used to collect organic vapors from the air after a Teflon filter has collected the particles. Sample XAD-01 was used in the Saudi Arabia sampling and sample XAD-06 was a laboratory blank, an unused sorbent tube. The used XAD was compared to the unused laboratory blank. The sample particulates collected on the PM-10 filters contained size segregated particles with aerodynamic diameters less than 10 μm . These particulates were collected on quartz fiber filters. A section of the filter was cut and mounted on a stub for analysis. The filter was searched in backscattered mode and high average atomic number particles were analyzed by Energy Dispersive Spectrometry (EDS). Approximately 20 particles per stage were analyzed by EDS.

The cascade impactor samples are size segregated by aerodynamic sizing which occurs during collection in the eight stage impactor. The stages of interest are MA-02-5, MA-02-6, and MA-02-7 with cut sizes 3.5, 2, and 1 μm respectively. These size particles are of particular interest because of their impact on respiratory health and visibility reduction. Substrates were searched in backscattered mode and high average atomic number particles were analyzed by EDS in an effort to identify any toxics or heavy metals. Approximately 10 particles were analyzed by EDS from each impactor substrate.

4.4.3 Results and Discussion

Analysis of the XAD sorbent media indicated that the surface appears smooth on both XAD-01 and XAD-06 and there was surface contamination on both types. The used sorbent (XAD-01) had more surface contamination (Figure 16) than the unused sorbent (Figure 17). This may have been the result of some small particles getting through the upstream filter. There was tweezer damage on both particle types which may contribute to the contamination. The interior appeared to have submicrometer structure and at 10 keV the exterior of the used (XAD-01) sorbent (Figure 18) appeared to be smoother than the unused (XAD-06) sorbent (Figure 19).

Analysis of the PM-10 filter samples suggested that the major particles were silicates and lead/bromine particles. Minor particles were barium particles and iron containing silicates. Figure 20 shows the loading of particles on the glass fiber filter. The EDS background of the quartz fiber filter is in Figure 21. Figure 22 is a typical lead/bromine particle EDS spectrum and Figure 23 shows a barium containing particle spectrum. A small agglomerate (primary particle size $\approx 0.5\text{--}1.0\ \mu\text{m}$) was identified by EDS as sodium and chlorine. Particles were difficult to pick out against the complex background of the fiber mat in secondary mode. The filter was searched in backscattered mode in order to simplify particle identification (Figure 24).

Analysis of the cascade impactor substrates, Mylar and stainless steel, provided a chance to compare the two materials for sample collection. Figure 25 is a low magnification view of the stainless steel substrate which in sharp contrast to the fiber filter (Figure 23) is well suited to electron microscopy. It has a much smoother surface, it is conductive, and particles are identified more easily. The Mylar substrate has the advantage of being even smoother with no background lines in the EDS spectrum, but it tends to charge under the beam in conventional scanning electron microscopy.



Figure 16. Micrograph of Used Sorbent Particle.



Figure 17. Micrograph of Unused Sorbent Particle.



Figure 18. Micrograph Showing Exterior Detail of Used Sorbent Particle



Figure 19. Micrograph Showing Exterior Detail of Unused Sorbent Particle



Figure 20. Loading of Particles on Glass Fiber Filter.

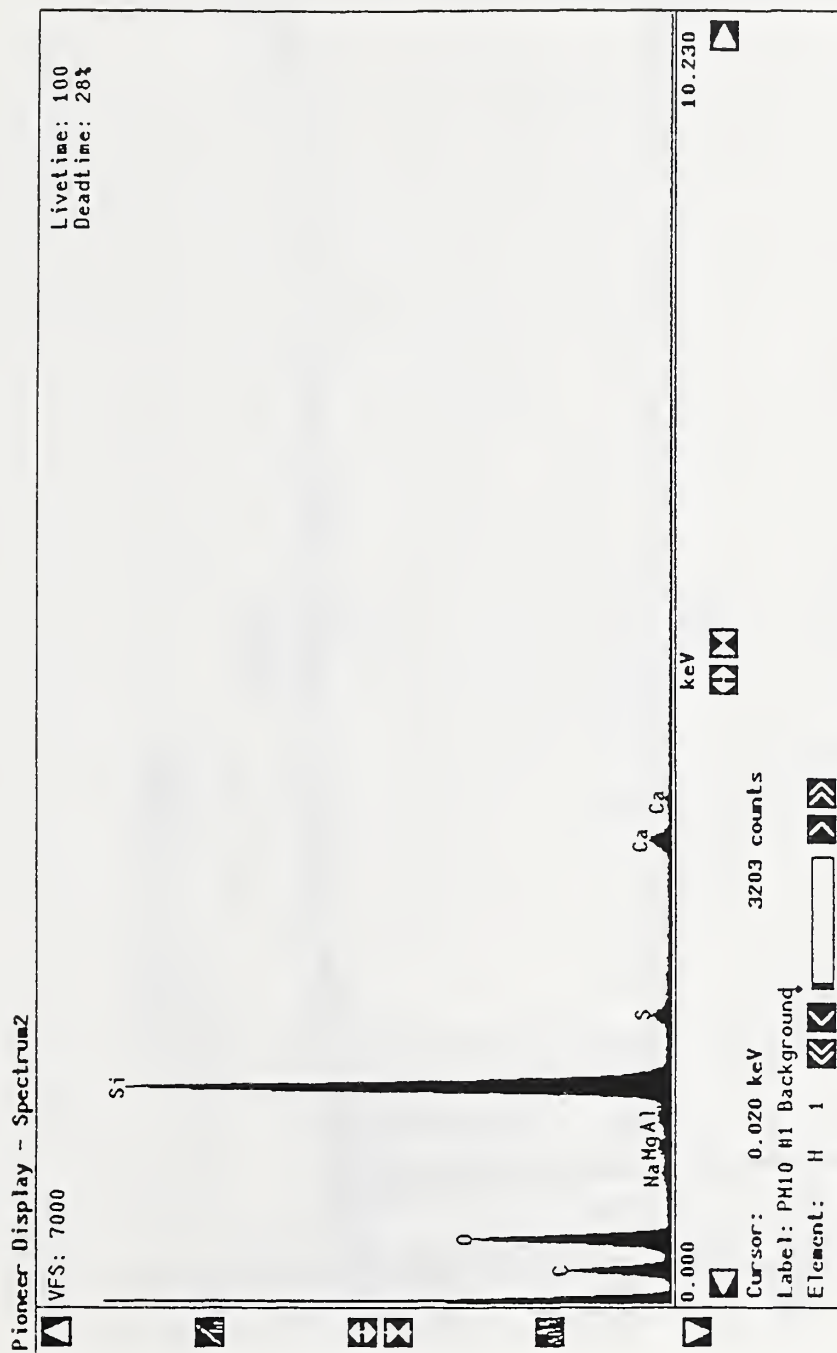


Figure 21. EDS Background of a Quartz Fiber Filter.

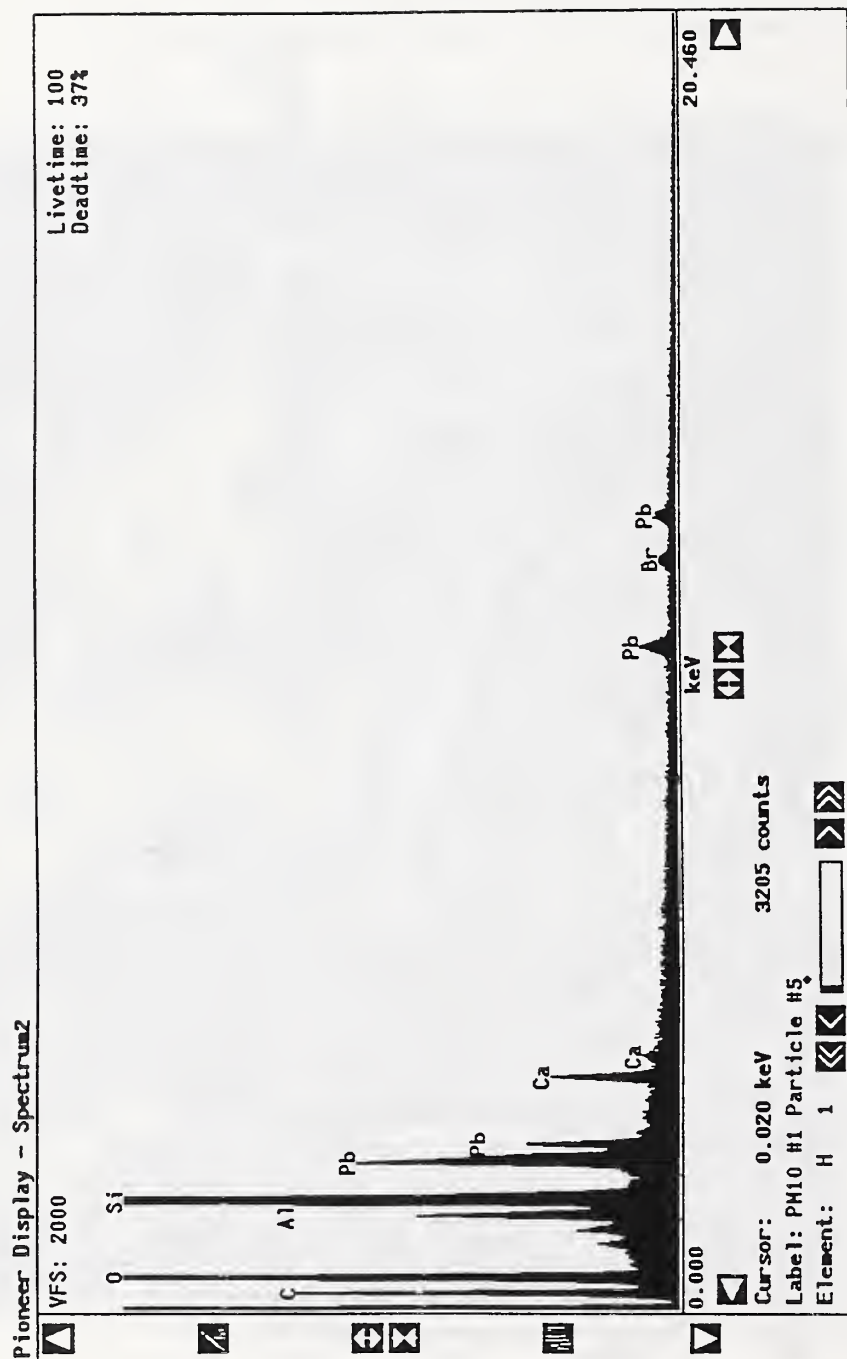


Figure 22. Typical Lead/Bromine Containing Particle EDS Spectrum.

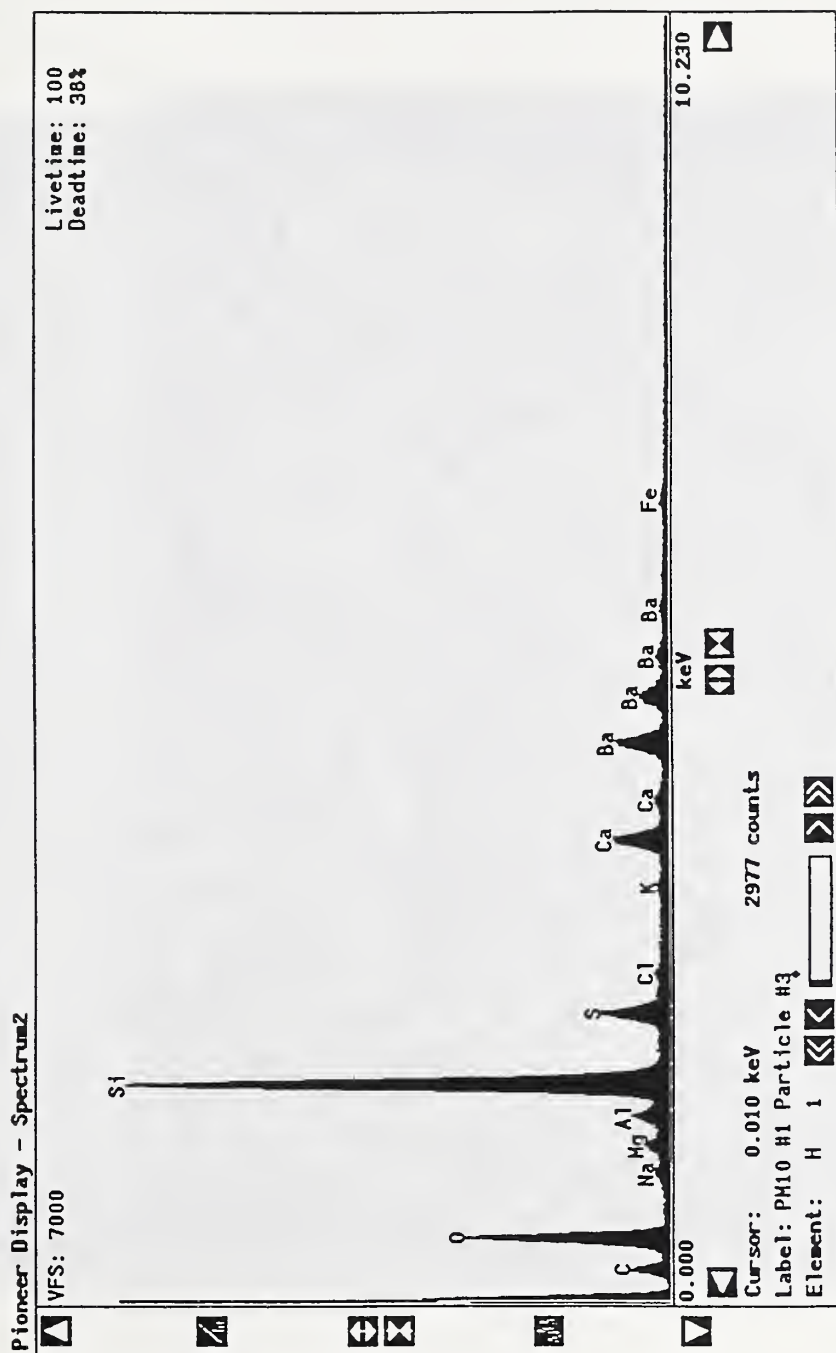


Figure 23. Typical Barium Containing Particle EDS Spectrum.

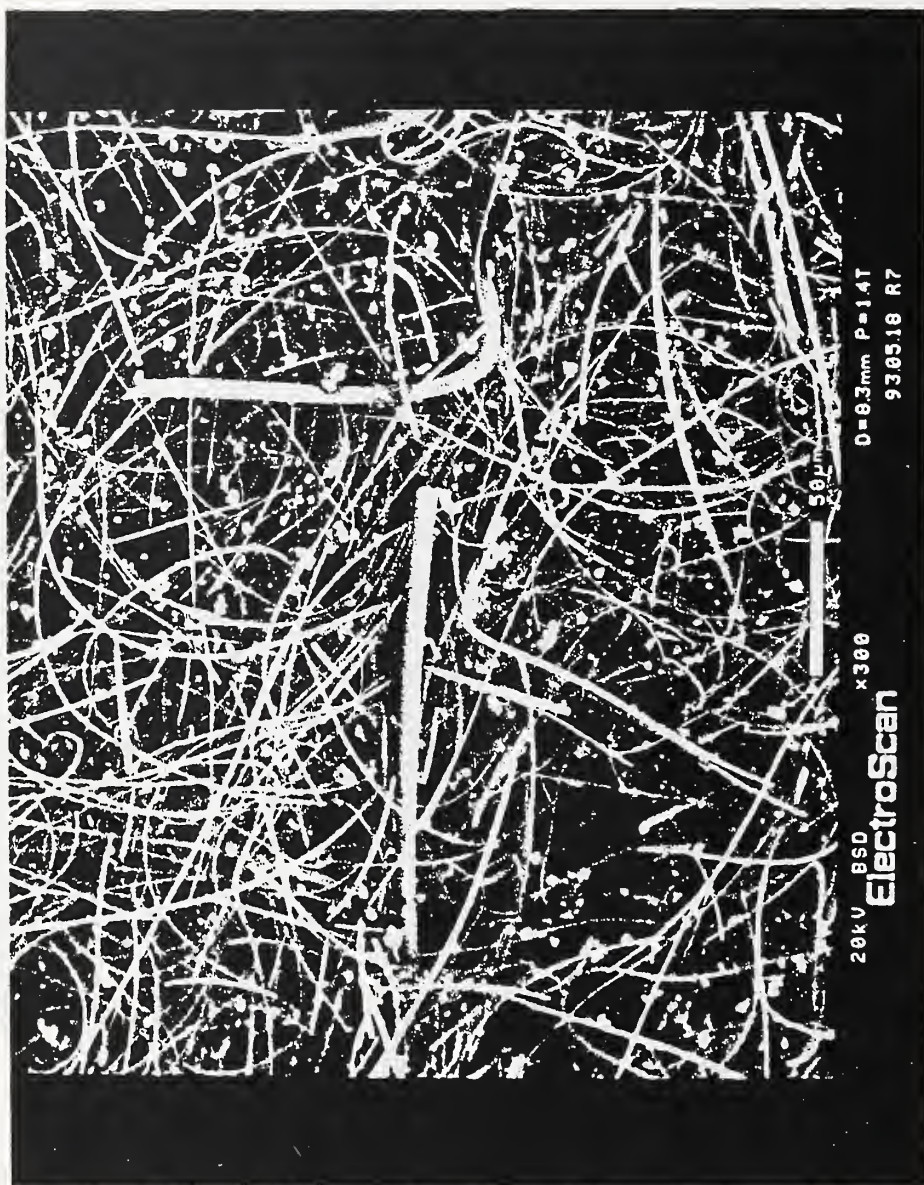


Figure 24. Backscattered Mode Search of Fiber Mat to Identify Particles.

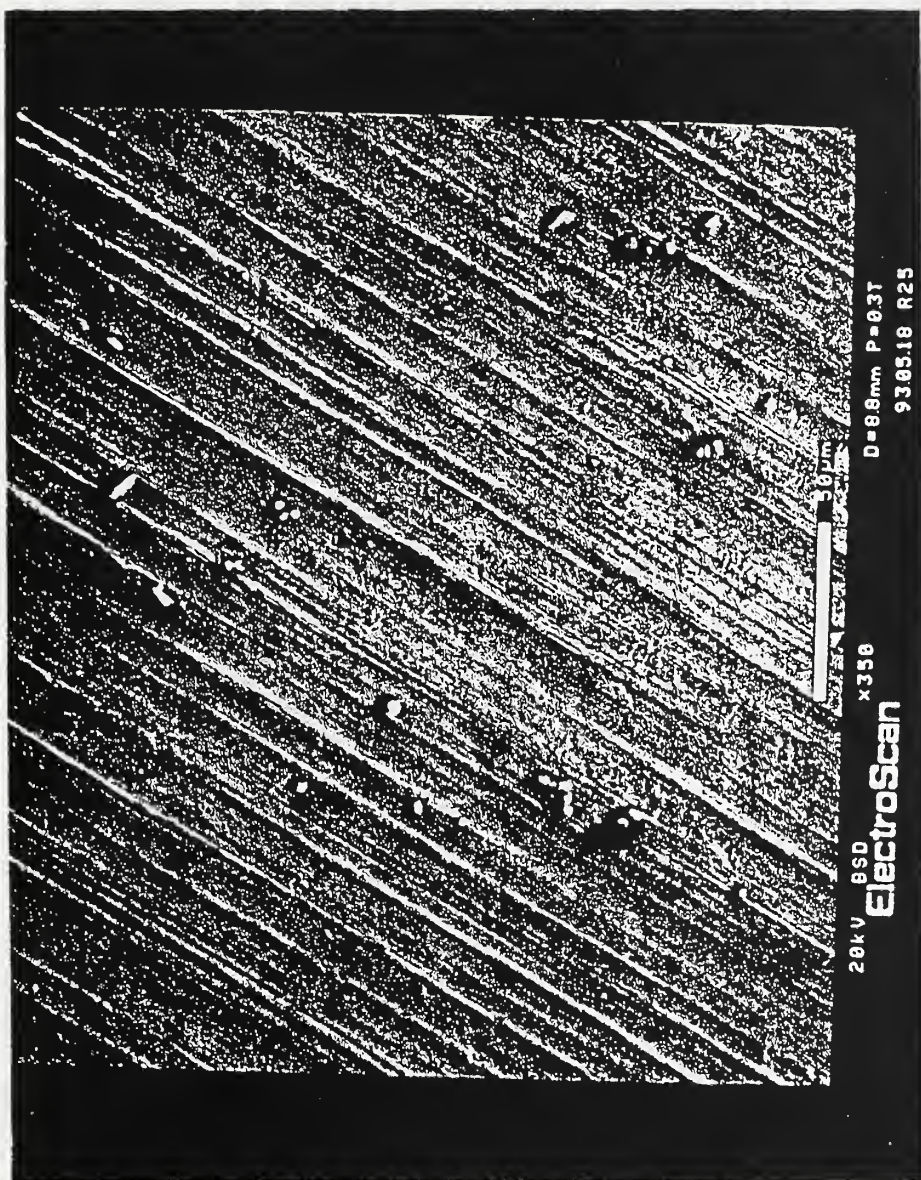


Figure 25. Low Magnification of Stainless Steel Substrate.

The stainless steel substrate, impactor stage 6 (MA-01-6) demonstrated mounds of silicate particles (Figure 26), most of which are irregularly shaped with sharp edges. A titanium-containing particle (Figure 27) was found on the surface of a silicate (Figure 28). A unique particle which had major phosphorus, sulfur, and oxygen and minor calcium, cerium, and titanium was found. EDS of the stainless steel substrate material yielded chromium, iron, nickel, and trace molybdenum (Figure 29). The sample loading on impactor stage 5 (MA-01-5), the second stainless steel substrate was very light. Calcium-containing and magnesium-aluminum-silicates made up the majority of the particles analyzed.

On the Mylar substrate MA-02-6, impactor stage 6, the majority of particles are silicates (Si, Mg, Al, Ca). Most of the particles were irregularly shaped with sharp edges. There was one particle with major titanium and four particles with iron and titanium. On the second Mylar sample, impactor stage 7 (MA-02-7), the particles appeared similar to other stages except the impact area was smaller and approached roundness. Calcium seemed to be the major element in these smaller particles.

In summary, the ESEM was particularly suited to the investigation of the PM-10 quartz fiber filters. The filter material is insulating and fibers tend to charge as in a conventional scanning electron microscope. The neutralization of surface charge in the low vacuum environment of the ESEM made it possible to analyze the particles directly on the filter.

There was a high concentration of mineral silicates of respirable size. Lead/bromine particles, presumably from gasoline burning, made up roughly five percent of the particles analyzed. Titanium/iron particles were much less abundant and may be mineral in origin.

4.5 Thermal-Optical Analysis For Organic/Elemental Carbon

Contributed by -
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4.5.1 Sample Preparation and Analysis

The current instrument is capable of analyzing aerosol particles for both organic carbon and elemental carbon. As with all current techniques, though, it is a method-defined analysis. However, it was designed to specifically address some of the problems seen by other techniques in assigning carbon to either the organic or elemental fraction. By careful control of operating conditions and constant monitoring of the optical absorbance of the sample during the analysis, this method is able to both prevent any undesired oxidation of original elemental carbon and make corrections for the inevitably-produced carbon-char formed by the pyrolytic conversion of some organics into additional elemental carbon.

The instrument is similar to that described by Johnson et al. [16]. However there are certain modifications, one being that the absorbance is monitored by transmitting the laser light through the sample filter rather than by observing the back-scattered light off the surface containing the sample deposit. Another is that the analysis starts at room temperature with pure helium and continues through four temperature steps (250, 385, 580, and 770 °C). The second stage of the analysis starts after reducing the temperature to 525 °C and introducing oxygen (2%). It then



Figure 26. Mounds of Silicate Particles.



Figure 27. Titanium Containing Particle.

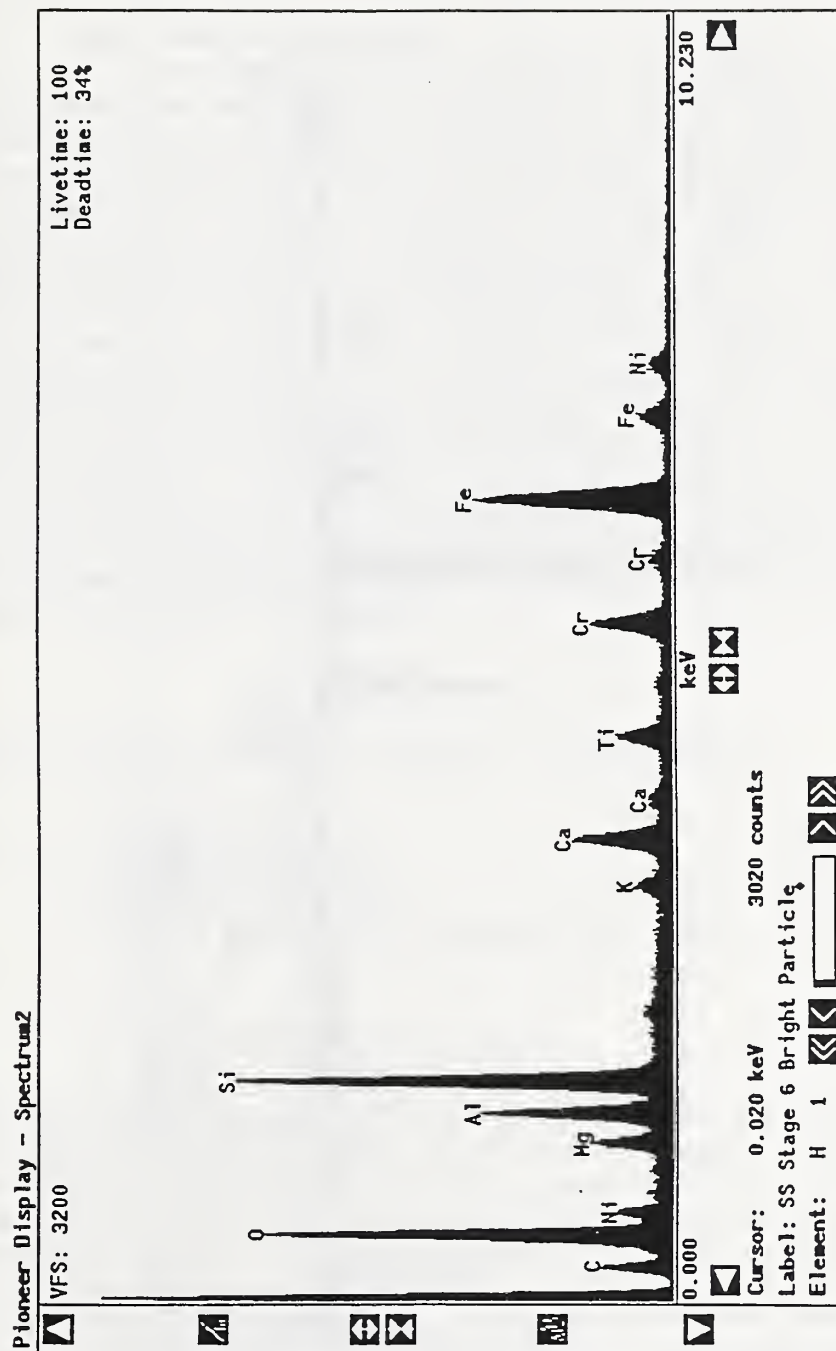


Figure 28. Surface of Silicate Particle.

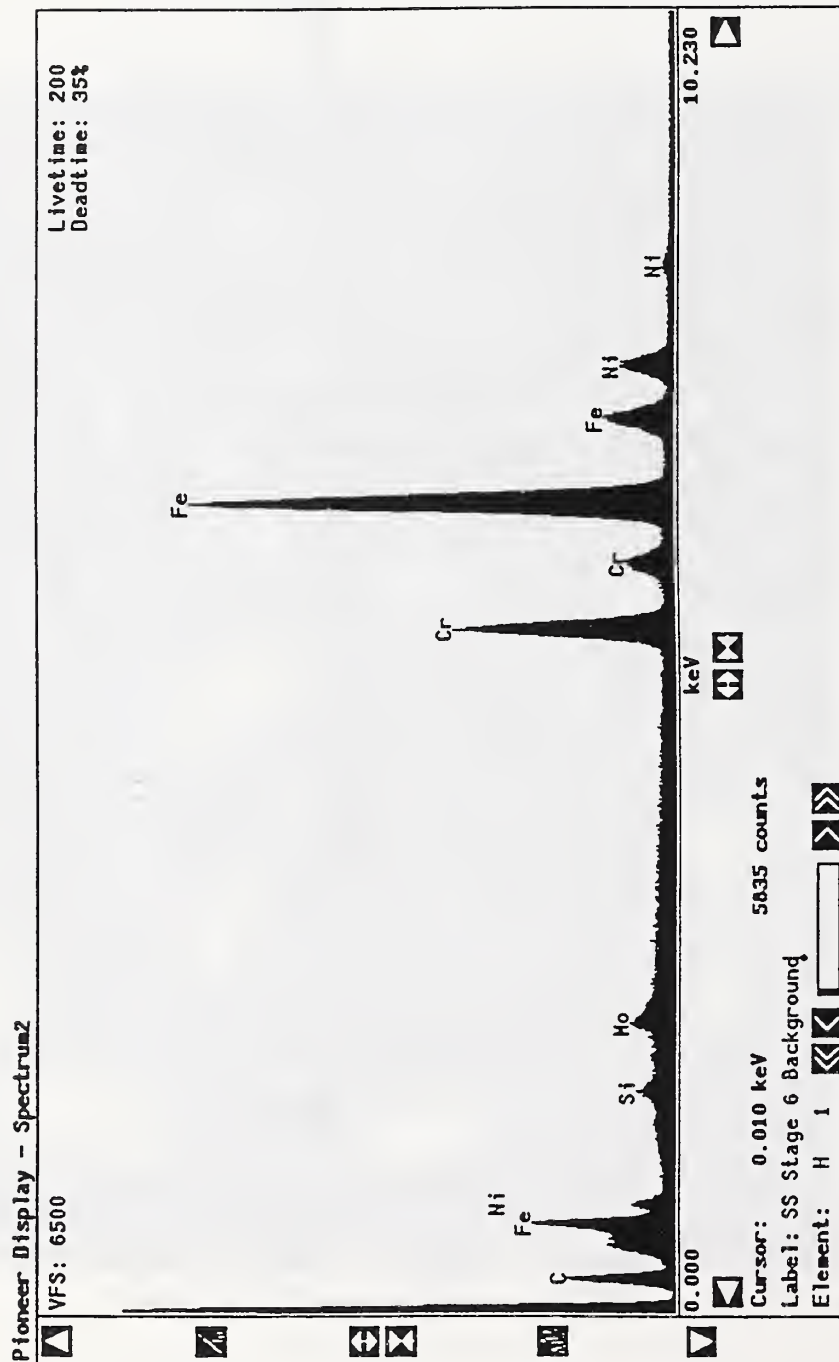


Figure 29. EDS of Stainless Steel Substrate.

continues with two more steps at 600 °C and 770 °C. The final part of the analysis is the injection of a known amount of methane which serves as an internal quantifying standard as well as a quality assurance step.

4.5.2 Results and Discussion

Each filter sample was analyzed for organic, elemental, and inorganic carbonate carbon. The organic carbon usually represents hydrocarbons which have simply evaporated from open liquid pools or have been partially pyrolyzed by a hydrocarbon fueled fire. Elemental carbon is suggestive of more complete combustion than the organic fraction. The inorganic carbonate content indicates that a fraction of the particulates probably originate from soil or sand. The fine sand or soil particles can be entrained by winds generated by the fire plume or simply by natural wind action.

Six quartz filter samples, PM-10-1, PM-10-2, PM-10-3, PM-10-4, Q-01, and Q-10 were analyzed for organic, elemental and inorganic carbonate content (Table 13). PM-10-1 and PM-10-2 were very similar in total carbon mass, 31.81 and 33.57 $\mu\text{g}/\text{cm}^2$. Both PM-10-1 and PM-10-2 were collected at KFMMC. Consistent with the lower PAH results, PM-10-3 had less total carbon mass, but total collection volume was also smaller than for PM-10-1 and PM-10-2. All three PM-10 samples exhibited approximately 27% elemental carbon/total carbon ratio. The inorganic carbonate fraction suggests that fine soil dusts contributed about 13% of the aerosol mass for the filters collected at KFMMC. Very little inorganic carbonate carbon was found on PM-10-3 which was collected at Al-Jubail. The 47 mm quartz filter, Q-01, produced similar organic mass loadings as the PM-10 filters, but elemental carbon appeared to be absent.

4.6 Gas Chromatographic Analysis of Grab-Bag Samples

Contributed by -
Mr. James E. Brown
Fire Science Division
Building and Fire Research Laboratory, NIST

4.6.1 Sample Preparation and Analysis

Two gas grab-bag samples, B-07 and B-06 were analyzed for carbon dioxide and carbon monoxide using a Hewlett Packard model 5890 Gas Chromatograph (GC) interfaced with HP 3396A Integrator. The GC was equipped with a thermal conductivity detector operated at 200 °C. The carrier gas was helium which flowed at 25 mL/min through a stainless steel column 183 cm long by 0.3175 cm outside diameter. The gas head pressure on the column was 160 kilopascals (22 psi). Separate columns, having the same dimensions, were used for the CO₂ and CO measurements. A column with Poropak N packing was used for the CO₂ analysis while the oven was operated. For the CO analysis a molecular sieve 5A column was used in the oven operated isothermally at 50 °C. The gas specimens were injected from either of two sample loops collected from a flow stream of the sample into the atmosphere and then injected onto the column through the injection port maintained at 150 °C.

Table 13. Organic/Elemental Carbon Analysis

Sample ID	Organic Carbon $\mu\text{g}/\text{cm}^2$	Organic Carbon Error	Elemental Carbon $\mu\text{g}/\text{cm}^2$	Elemental Carbon Error	Inorganic Carbon $\mu\text{g}/\text{cm}^2$	Total Carbon $\mu\text{g}/\text{cm}^2$	EC/TC Ratio
PM10-1	18.67	1.24	9.04	0.55	4.10	31.81	0.284
PM10-1 Repeat	19.64	1.29	8.72	0.54	4.20	32.56	0.268
PM10-2	20.19	1.31	9.28	0.56	4.10	33.57	0.276
PM10-3	8.96	0.55	3.16	0.26	0.10	12.22	0.259
PM10-4 Blank	0.95	0.15	-0.09	0.10	0.00	0.86	-0.106
Q1	1.71	0.19	0.00	0.10	0.00	1.71	-0.001
Q10 Blank	0.38	0.12	-0.03	0.10	0.00	0.35	-0.085
OC - Organic Carbon EC - Elemental Carbon CC - Inorganic Carbonate Carbon (values are estimated) TC - Total Carbon							

The responses of the TCD and retention times of the CO₂ and CO in the respective columns were determined using a reference gas containing 798 ppm CO₂ and 407 ppm CO in nitrogen. At least 10 specimens of this gas were injected into the respective column to determine the TCD calibrations. Response data for calibration were used after the detector indicated that all air had been swept from the sample lines. This usually required 3 to 5 injections.

After establishing the TCD response and calibrating the TCD with a reference gas, the two grab-sample bags were analyzed first for carbon dioxide and then for carbon monoxide.

4.6.2 Results and Discussion

The results of gas chromatographic analyses of two grab samples of air for carbon dioxide and carbon monoxide are shown in Table 14. The concentrations of carbon dioxide in both samples were about 0.036 percent. Although routine monitoring of CO₂ would help to establish the range of background levels, these concentrations do not appear to be significantly above the 0.033 percent [17] levels generally accepted for ambient air. Carbon monoxide was not detectable in either of the grab-bag samples. Since CO and CO₂ are products of combustion, both of these two gases would be expected to be elevated in a cloud or plume generated by a fire. Since the samples collected at KFMMC Dhahran and RSNB Al-Jubail at relatively ambient conditions, i.e., not in a plume or near a fire source, it was not surprising that the CO and CO₂ were not significantly higher than background levels. However, additional sampling and a routine monitoring program would be important to establish better what typical background levels are within the Kingdom.

5.0 Discussion

Sample analyses including polycyclic aromatic hydrocarbon, laser microprobe mass spectrometry, micro-Raman analysis, environmental scanning electron microscopy, thermal-optical analysis, and gas chromatography provide a snapshot of the physical and chemical properties of the aerosol sampled at KFMMC and RSNB. This very limited snapshot of the aerosol around KFMMC and RSNB does not provide a reasonable basis for estimating the short- or long-term health risk due to exposure to smoke and gaseous emissions. While these results do suggest significant levels of PAH and dust particulates, the data set is very limited and a program involving the collection and analysis of air samples (HiVol PM-10) in or around Saudi Arabian urban areas, such as Riyadh, Al-Jubail, and Dhahran, would provide valuable data for determining current airborne PAH concentrations as well as for devising air pollution control strategies for the future.

Most of the short-term exposure samples which were collected over a relatively short time period do not suggest significant levels of smoke or gaseous species. The PAH analysis of the Teflon filters and XAD-2 sorbent tubes, the CO and CO₂ analysis of the grab-bag samples, and the thermal-optical analysis of the quartz filters all suggest that the concentrations of PAHs, CO, and CO₂ were not significantly elevated above background levels. But, one of the quartz filters, Q-05, did collect significant amounts of particulates. Other results suggest that most of these particulates were fine soil dust. These samples, which were collected during a dust storm, indicate relatively high levels, 3 mg/m³, of total particulates; and probably a high fraction of the particulates were classified as inhalable. The observed particulate concentrations are about half the Occupational Safety and Health Administration standards for respirable nuisance dust, 5 mg/m³, but are approximately 50 times

Table 14. Gas Chromatographic Analysis of Grab-Bag Samples

Sample ID	Carbon Dioxide Concentration (ppm)	Carbon Monoxide Concentration (ppm)	Collection Location
B-06	368	not detected	KFMMC Dhahran
B-06 Repeat	366	not detected	
B-06 Repeat	366	not detected	
B-08	362	not detected	RSNB Al-Jubail
B-08 Repeat	361	not detected	
B-08 Repeat	362	not detected	
RSNB - Royal Saudi Naval Base Hospital Roof, Al-Jubail KFMMC - King Fahad Military Medical Center Roof and Apartment Roof, Dhahran			

greater than the National Institute of Occupational Health and Safety Standard for respirable crystalline silica, 0.05 mg/m^3 [18]. A qualified medical specialist would use the total particulate concentration, the respirable fraction, and the chemical composition of the particles to assess the potential health risk to the local population.

In addition to the dust collected on the quartz filter, several of the samples collected at KFMMC during the dust storm had observable amounts of reddish-tan particulates on the filter. The results of analysis by Laser Microprobe Mass Spectrometry indicate that the reddish-tan particulates are primarily inorganic fine dust particulate material. This material appears to be fine particle matter that is composed of Na, Mg, Al, Si, K, Ca, Fe, Ti, and some Ba. The particles found on the quartz fiber filter contained lead. As reported in the PAH analyses of the reddish-tan particulates, there appears to be very little carbon molecular species present in the samples analyzed. The ESEM examination indicated that there was a high concentration of mineral silicates of respirable size. Lead/bromine particles, presumably from leaded gasoline combustion, made up roughly five percent of the particles analyzed. Titanium/iron particles were much less abundant and may be mineral in origin. The inorganic carbonate fraction reported by the thermal-optical analysis suggests that fine soil dusts contributed about 13% of the aerosol mass for the PM10 filter samples collected at KFMMC.

While most of the PAHs were essentially not detectable for the Teflon filters and XAD-2 sorbent tubes, the PAH analysis of the PM-10 filters detected significant levels of the higher molecular weight PAHs. This was not unexpected because the PM-10 HiVol samplers are ambient monitors and PAH sampling trains are usually employed for more acute episodes. The HiVol samplers pull between 1000 and 1500 liters through the PM-10 filter each minute while the portable pumps pull about 2 liters per minute through the PAH sampling train. In order to accumulate sufficient material to be easily detected by standard analytical techniques, the HiVol samplers are designed to sample and filter very large volumes of aerosol. The portable pump and PAH sampling train allow sampling the high concentration of PAHs in a smoke plume or cloud. But, both the PM-10 HiVols and the portable systems are important components to an air monitoring program. The ambient samplers collect routine samples for archival background purposes and the portable pump and PAH sampling train help characterize more acute episodes.

The results of the thermal-optical analysis show the same trend as the PAH results. The thermal-optical results suggest that from 60 to 70 percent of the carbon on the PM-10 filters was organic, but very little organic carbon was observed on the 47 mm quartz filters. Again, the organic carbon, including the PAH compounds, were detected on the relatively large volume PM10 samples, but not on the quartz filters which sampled a small volume. Overall, the different analytical techniques all help to characterize the physical and chemical properties of the aerosol sample around Dhahran and Al-Jubail. As in the case of the high levels of dust particulates, the particulate sampling and sizing instrumentation demonstrated that it is possible to quickly determine particulate mass concentrations. The particulate samples were then returned to the laboratory for more specialized analysis which helped to confirm the source of the fine particulates. The appearance of significant concentrations of PAHs in what was expected to provide background levels indicates that a more comprehensive sampling program should be implemented to characterize the levels and the distribution of PAHs throughout the Kingdom.

6.0 Conclusions

The gas and aerosol particulate samples collected in Saudi Arabia by the MODA and NIST researchers demonstrates that NIST through the training course and collaborative sampling work was able to provide MODA personnel with the tools to begin local monitoring of smoke and gaseous emissions. Ranging from simple gravimetric weighing to laser micro-probe techniques, the analytical methods successfully illustrated what types of chemical and physical information can be extracted from smoke and gas samples. MODA personnel have obtained the necessary skills to initiate a local monitoring and sampling program.

The limited number of smoke and gas samples collected does not provide an adequate data set to determine the health risks to the population. Establishing short- and long term health effects on population groups was beyond the scope of this limited project which was designed to provide MODA personnel with the tools to collect their own samples. The results of this project do indicate that additional samples do need to be collected to allow a better assessment of the type and distribution of PAHs, gases, and particulates throughout Saudi Arabia.

7.0 Recommendations

The NIST visitors and the RAFMH personnel discussed the implementation of a program involving the sampling of air in Saudi Arabia and the subsequent measurement of health-related species. A program could be divided into:

- Developing a plan for monitoring particulate matter and gas concentrations;
- Collect and archive particulate matter and gas samples;
- Develop analytical methodology for measuring specific sample constituents in order to determine their toxicological significance;
- Implement quality control program to insure high confidence in data.

7.1 Planning

Any planning for this project should involve a thorough search of the technical literature so that all the subsequent aspects of the project, from sample collection and analysis to data analysis are carefully researched. There are currently a number of on-line computer databases including Chemical Abstracts (from the American Chemical Society), Environmental Abstracts and Analytical Abstracts that could be used to obtain literature citations supporting the sampling and analysis of airborne pollutants. In addition, CA Selects from the American Chemical Society offers subscriptions for bi-monthly computer searches of a number of topics related to atmospheric chemistry (e.g., Environmental Pollution, Air Pollution - Books and Reviews, Pollution Monitoring, Indoor Air Pollution). Using these databases is an good way of determining what work has been done in an area of interest, how the work was done and what additional research needs to be performed to solve the problem and/or complete the project. Reviewing the appropriate literature prior to beginning a project lessens the chance that time will be wasted developing a method or technique that has already been thoroughly evaluated.

7.2 Sample Collection

The RAFMH group has already collected a number of air samples in Dhahran and Al-Jubail using their new air sampling equipment. Some of the equipment is useful for collecting ambient inhalable particulate matter (IPM, PM-10 Hi-Vol samplers) for later measurement of IPM and organic/inorganic compound concentrations. Other pieces of equipment would be useful in measuring gases (EXOTOX gas meters) and particles (MINIRAM particle counters) under acute pollution situations such as might occur indoors and/or very near a fire. Since the RAFMH group now has PM-10 samplers, it is recommended that permanent monitoring sites be established in the Riyadh vicinity to obtain samples for IPM determinations. These samples could then be stored in freezers for later measurements of organic (PAHs) and inorganic species (heavy metals, organic/inorganic carbon) once the appropriate methods are developed. These data will be useful in establishing baseline concentrations of IPM and chemical species in the Riyadh atmosphere. Purchase of additional PM-10 samplers would be desirable in order to establish a comprehensive sampling network around Riyadh as well as for equipping mobile air sampling systems.

7.3 Sample Analysis

There are a number of established techniques for measuring organic and inorganic species in the atmosphere. The PAHs, for example, can be measured by spiking the sample with a standard containing perdeuterated PAHs, extracting the sample with dichloromethane and measuring the PAHs by GC-MS. Important considerations in such measurements include filter blank concentrations, detection limits and IPM sample loading.

7.4 Quality Assurance

For such method development at RAFMH, it would be advisable to purchase standard samples that have been thoroughly characterized for PAHs. The NIST offers a number of Standard Reference Materials (SRM) that are useful in validating analytical methods for PAHs and other chemical species. By processing the appropriate SRM through one's analytical scheme and comparing the results with those in the SRM's Certificate of Analysis, one can decide if the method is valid and that the data obtained is of the highest quality.

7.5 Split Sample Analysis

In the early stage of an air monitoring program, it may be useful to split the collected samples with a laboratory established in the field for airborne pollutant measurement. This along with analysis of appropriate reference materials (e.g., SRMs), would help insure that the data generated would be of the highest quality possible.

Appreciation

We wish to thank Lt. Colonel Al-Nasser for all the arrangements of accommodations, transportation and use of facilities in Riyadh, Dhahran and Al-Jubail. We are also much appreciative of Captain Al-Hedaithy, Lieutenant Kholafy and Mr. Al-Asmari for their valuable help during the field sampling. Finally, we would like to thank Lt. Colonel Al-Nasser and Mr. Al-Asmari for detailed discussion concerning the formation of a center for monitoring health-related compounds in the atmosphere over Saudi Arabia.

We have very much enjoyed visiting Riyadh and the RAFMH and look forward to collaborating with RAFMH in the future. We hope to be able to provide additional input for the future establishment of the environmental aerosol and gas monitoring center.

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APPENDIX A.

Ground-Based Smoke Sampling Course Program

The schedule for training MODA personnel to monitor particulate concentration and size, gas concentration, hydrocarbons, metals and metal salts will include:

Day 1 Introduction

- Health Effects
- MEPA and EPA Guidelines
- Combustion Fundamentals

Inhalable Particulates - Total Mass Concentration

- Light Scattering Cell
- Calibration
- Operation
- Gravimetric Measurement
- Portable Pump
 - Flow Calibration
 - Operation
- Filter Media
- Mettler Balance Operation

Day 2

- Inhalable Particulates - Size Classification of Aerosols
- Aerodynamic Sizing Theory
- Personal Samplers
- Marple Personal Cascade Sampler
- Anderson Cascade Impactor
- Ambient Samplers
- High Volume PM10 Samplers
- Data Reduction and Presentation

- Chemical and Optical Properties of Smoke
- Organic versus Elemental Carbon
 - Black Sooty Smoke
 - Grey Pyrolysis Smoke
- Light Extinction
 - Absorption, Scattering and the TC-RN

Gas Analyzers - Personal Monitors
Fundamentals of Electrochemical Cells
Portable Analyzers
Multi-Gas Monitors
Calibration
Operation
Single Gas Analyzers
Calibration
Operation

Day 3

Gas Sampling
Grab Bags
Sample Collection
Sample Analysis
Sorbent Tubes
Sample Collection
Sample Analysis

Hydrocarbon Monitoring
TUH Analyzers
Polycyclic Aromatic Hydrocarbons
Filter Samples
Preparation
Collection
Storage
Analysis
Sorbent Tube Samples
Collection
Analysis
Volatile Organic Hydrocarbons
Collection
Analysis

Metal Sampling and Monitoring
Filter Samples
Substrate Preparation
Sample Collection
Analysis via Neutron Activation

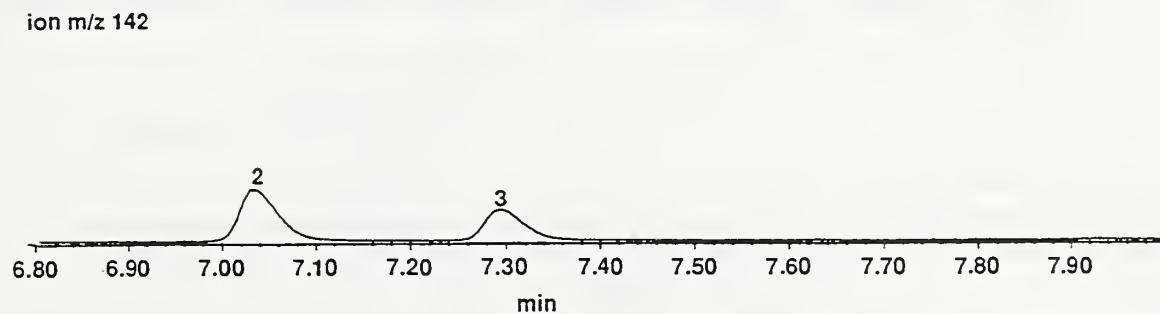
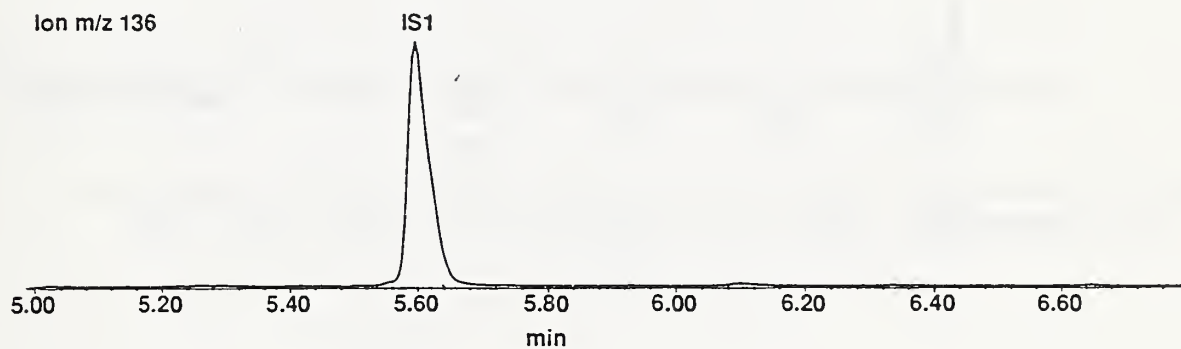
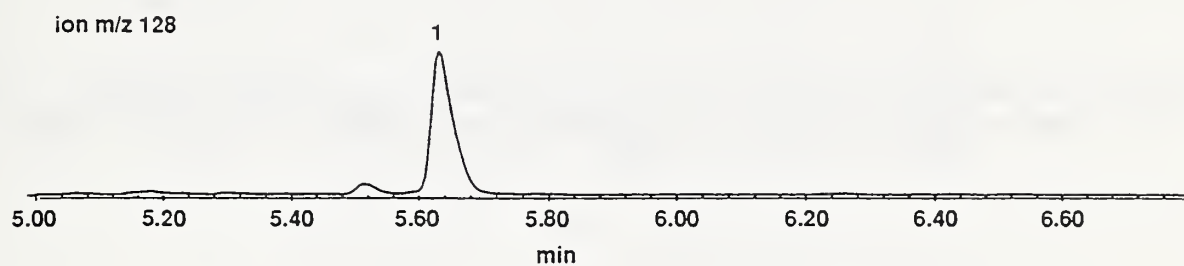
Day 4	<p>Fire Test - Crude Oil Burn</p> <ul style="list-style-type: none"> Preparation for smoke sampling Filter Weighing Gas Analyzer Calibration Pump Check-out Real-time Measurements Total Mass Concentration Sulfur Dioxide Nitrogen Dioxide Hydrogen Sulfide Carbon Monoxide Carbon Dioxide Samples for Laboratory Analysis Total Mass Concentration Size Classified Particulates Organic versus Elemental Carbon Gas Grab Bag Sampling PAH Filter Samples Sorbent Tubes VOC Sorbent Tubes Sample Storage Data Reduction Filter weighing
Day 5	<p>Fire Test - Crude Oil Burn</p> <ul style="list-style-type: none"> Same as Day 4 - more practice in field sampling
Day 6	<p>Analytical Chemistry -</p> <ul style="list-style-type: none"> Sample preparation Gas chromatography Theory Analysis of grab bag samples Data Interpretation
Day 7	<p>Analytical Chemistry</p> <ul style="list-style-type: none"> Sample preparation Liquid Chromatography Theory

Analysis of Filter Samples
Analysis of Sorbent Tube Samples
Data Interpretation

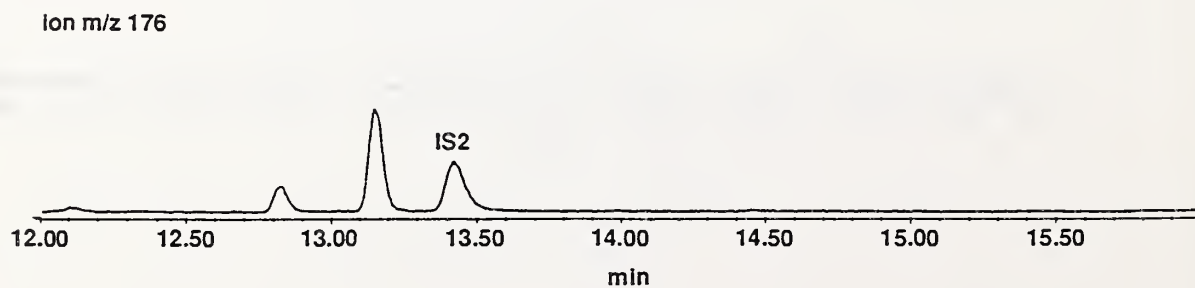
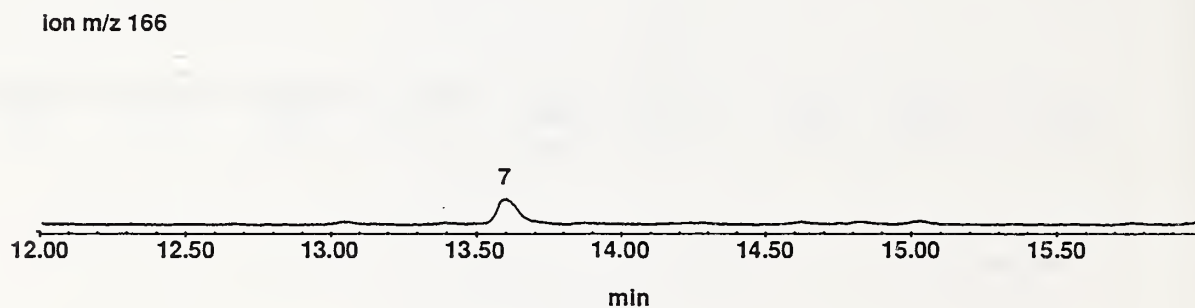
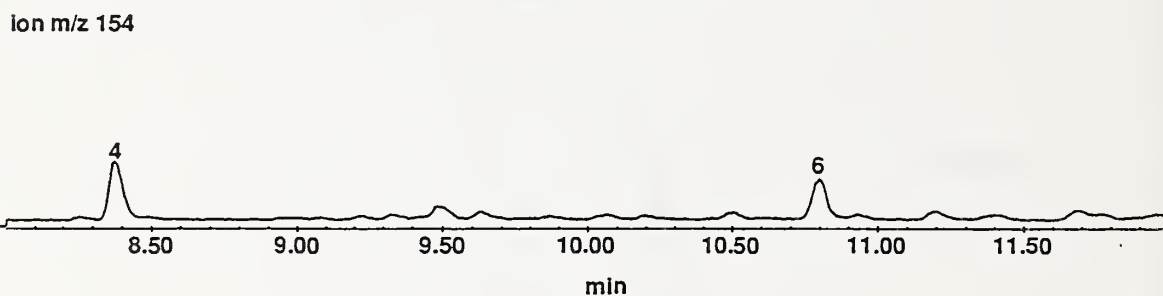
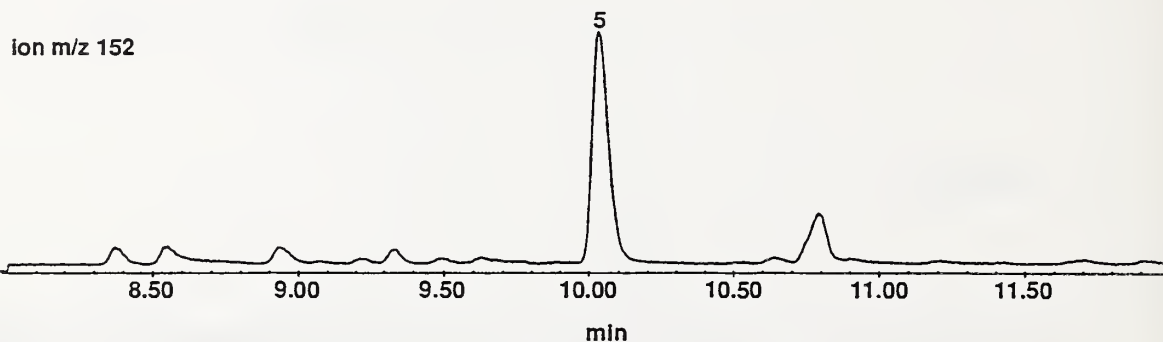
Day 8

Review

APPENDIX B. Reconstructed Selected-Ion Chromatograms of Sorbent Tube Sample XAD-01
Collected at the Royal Saudi Naval Base (See Table B-1 for peak identification)



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Collected at the Royal Saudi Naval Base (See Table B-1 for peak identification)

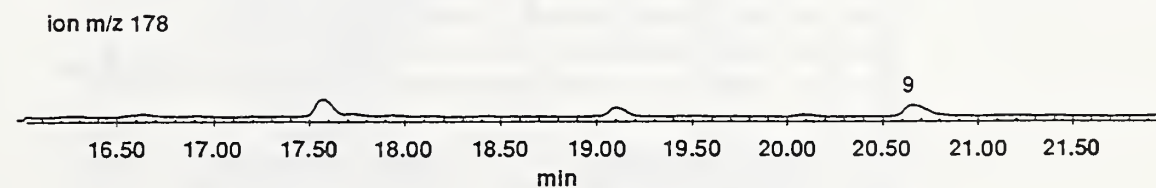
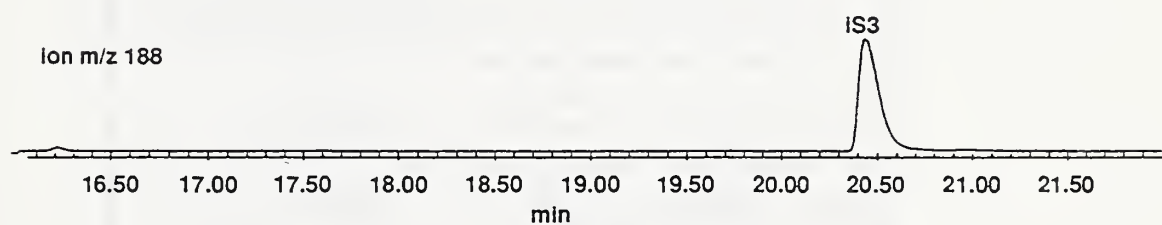
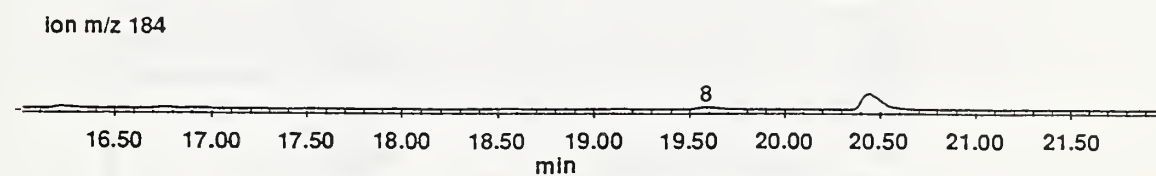
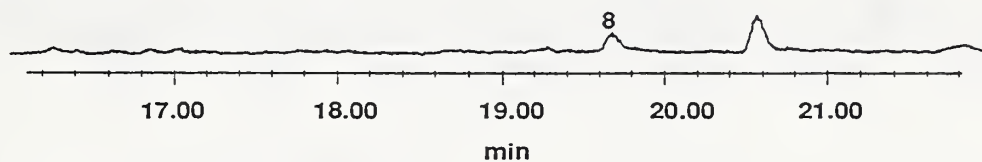


Table B-1. Peak Identifications for Reconstructed Selected-Ion Chromatograms of Sorbent Tube XAD-01.

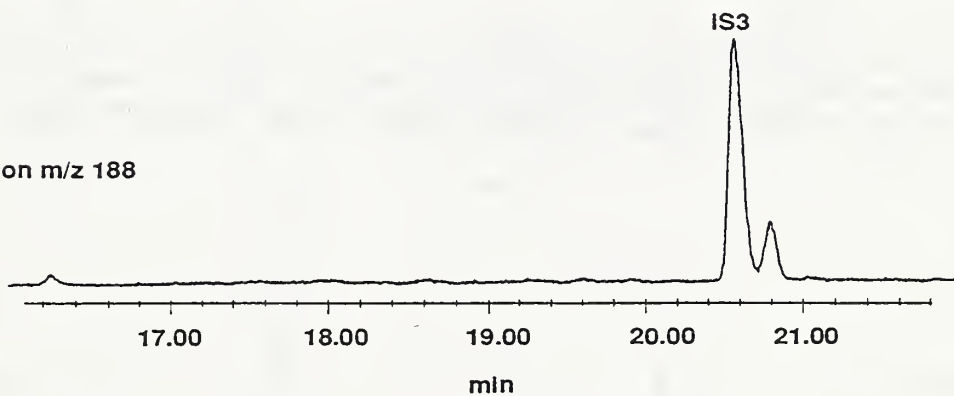
Peak Number	Polycyclic Aromatic Hydrocarbon (PAH)
1	naphthalene
IS1 (Internal Standard)	naphthalene-d ₈
2	2-methylnaphthalene
3	1-methylnaphthalene
4	biphenyl
5	acenaphthylene
6	acenaphthene
7	fluorene
IS2 (Internal Standard)	fluorene-d ₁₀
8	dibenzothiophene
IS3 (Internal Standard)	phenanthrene-d ₁₀
9	phenanthrene
10	anthracene
11	4,5-methylenepheneanthrene
10	3-methylphenanthrene
10	2-methylphenanthrene
10	4- and 9-methylphenanthrene
15	1-methylphenanthrene
16	fluoranthene
17	acephenanthrylene
15	pyrene
IS6 (Internal Standard)	pyrene-d ₁₀
10	benz[a]anthracene
20	triphenylene
20	chrysene
IS5 (Internal Standard)	benz[a]anthracene-d ₁₂
22	benzo[b]- and benzo[j]fluoranthene
23	benzo[k]fluoranthene
24	benzo[a]fluoranthene
25	benzo[e]pyrene
26	benzo[a]pyrene
27	perylene
IS6 (Internal Standard)	benzo[k]fluoranthene-d ₁₂
IS7 (Internal Standard)	benzo[e]pyrene-d ₁₂
28	indeno[1,2,3-cd]pyrene
29	benzo[ghi]perylene
IS8 (Internal Standard)	benzo[ghi]perylene-d ₁₂

APPENDIX C. Reconstructed Selected-Ion Chromatograms of HiVol Filter Sample PM10-01
Collected at the King Fahad Military Medical Center
(See Table C-1 for peak identification)

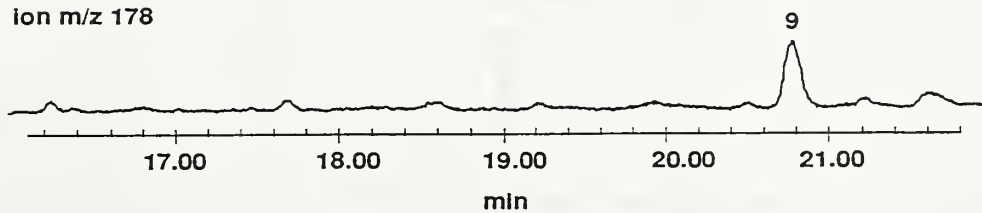
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ion m/z 188

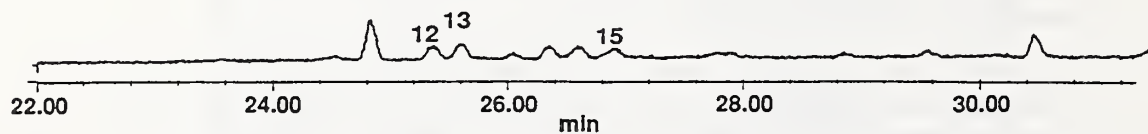


ion m/z 178

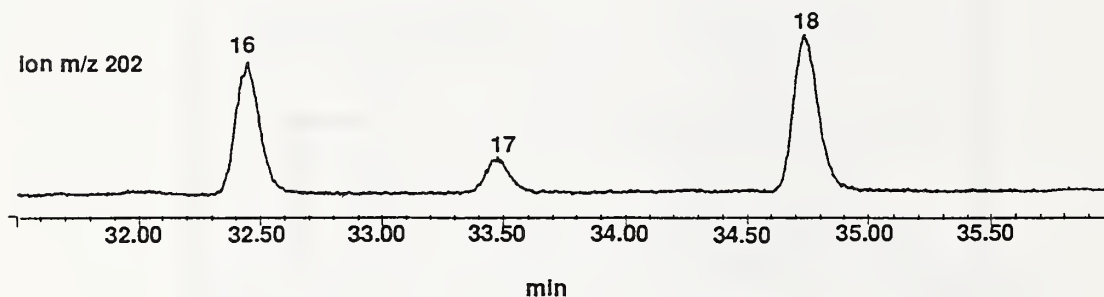


APPENDIX C. Reconstructed Selected-Ion Chromatograms of HiVol Filter Sample PM10-01
Collected at the King Fahad Military Medical Center
(See Table C-1 for peak identification)

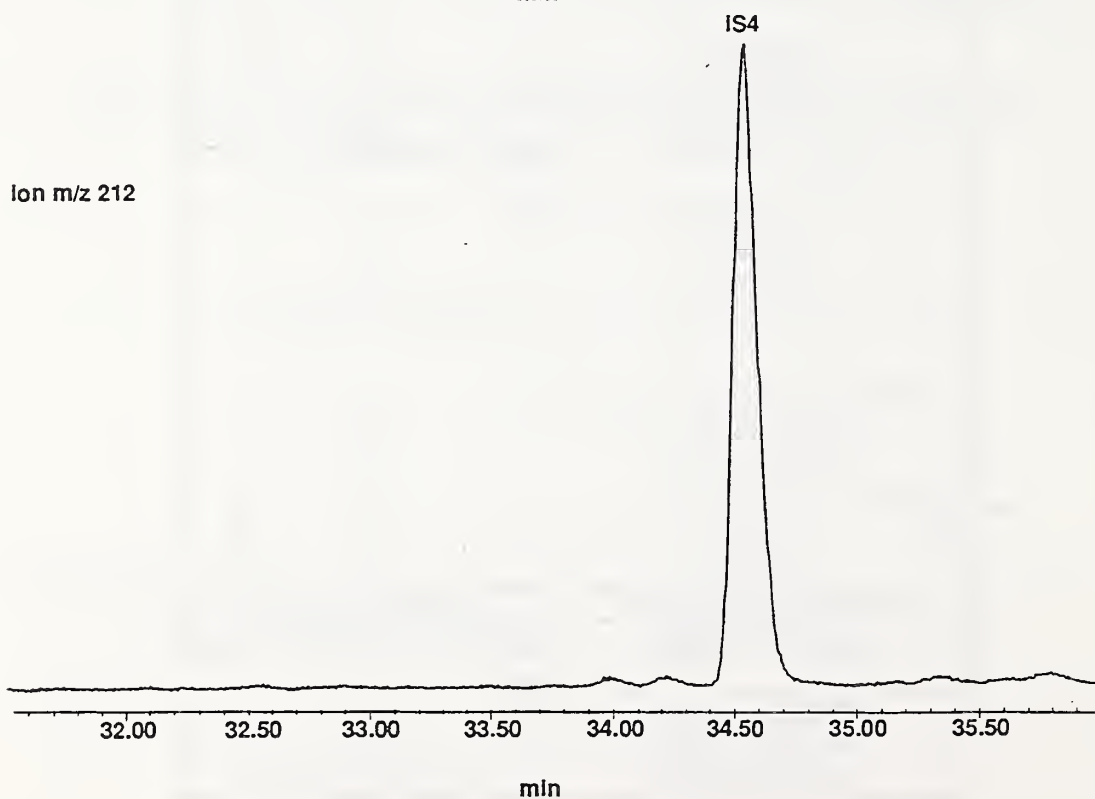
Ion m/z 192



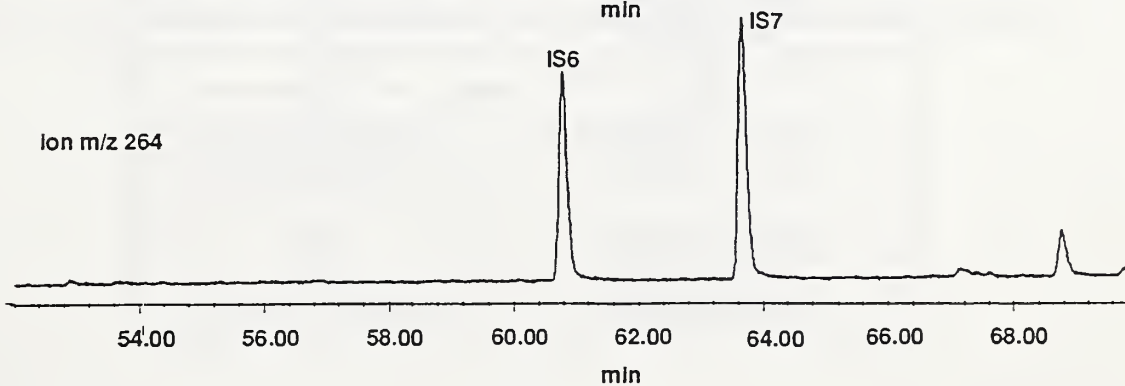
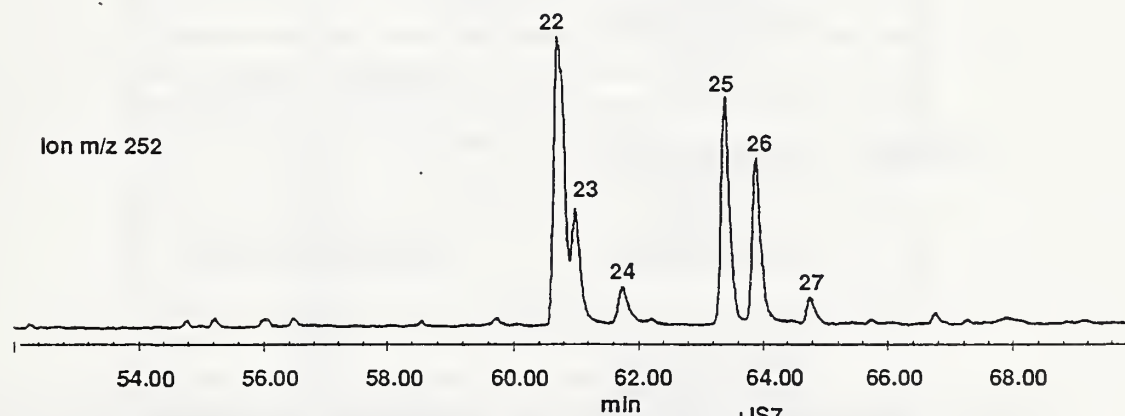
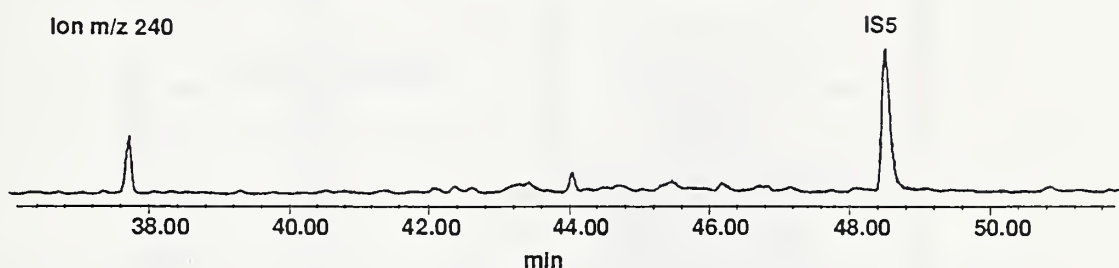
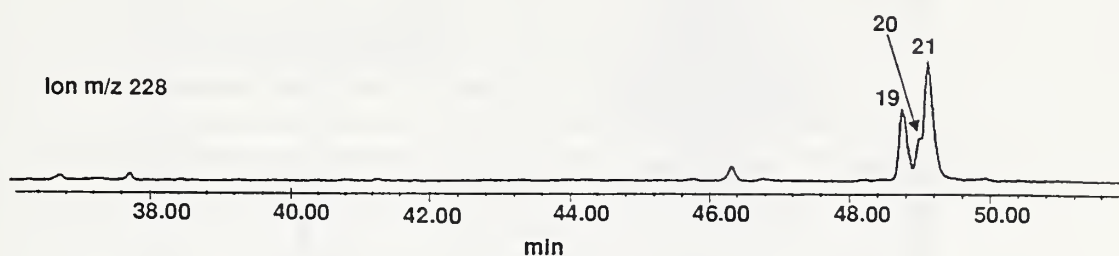
Ion m/z 202



Ion m/z 212



APPENDIX C. Reconstructed Selected-Ion Chromatograms of HiVol Filter Sample PM10-01
Collected at the King Fahad Military Medical Center
(See Table C-1 for peak identification)



APPENDIX C. Reconstructed Selected-Ion Chromatograms of HiVol Filter Sample PM10-01
Collected at the King Fahad Military Medical Center
(See Table C-1 for peak identification)

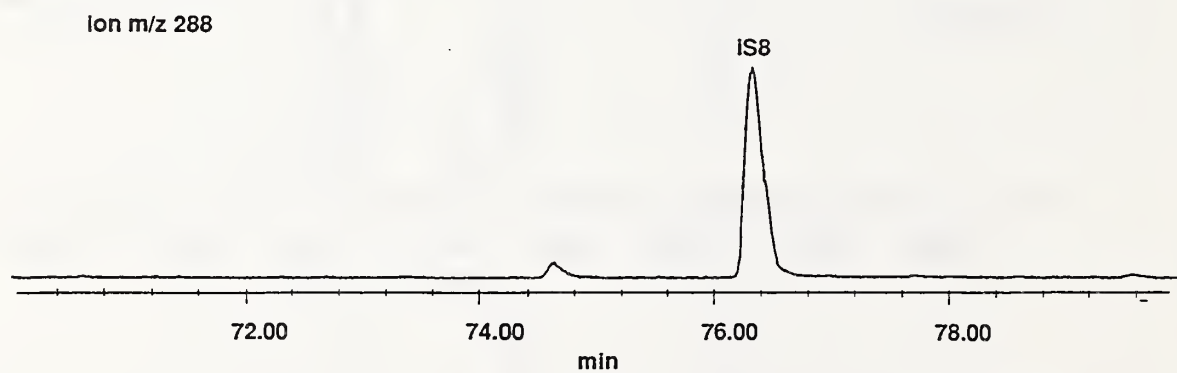
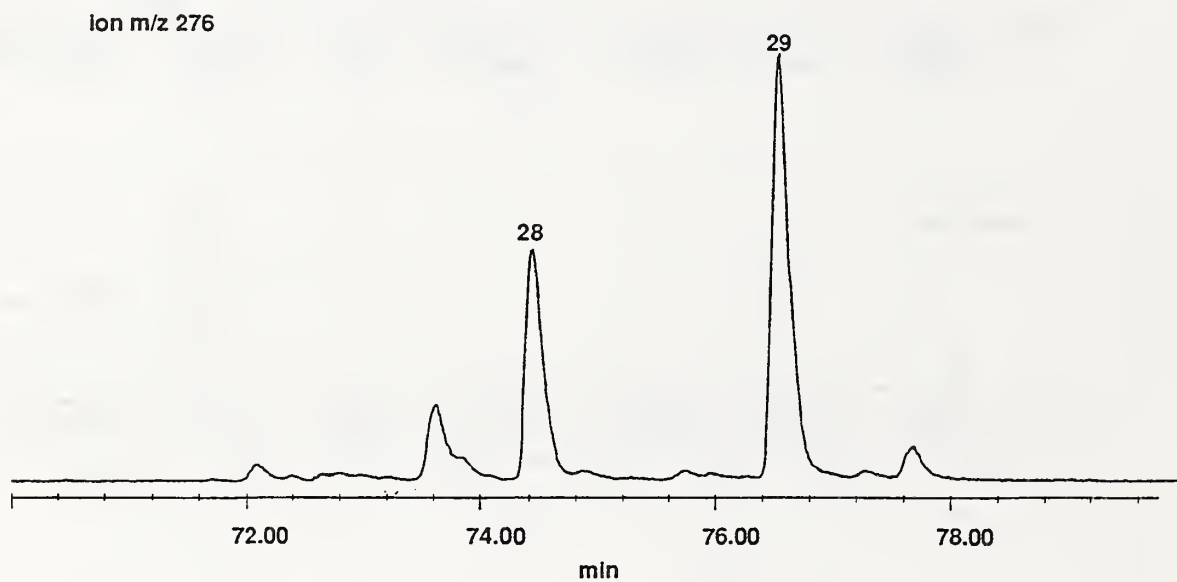
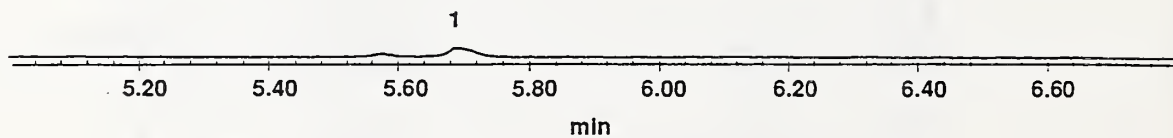


Table C-1. Peak Identifications for Reconstructed Selected-Ion Chromatograms of HiVol Filter PM-10-1.

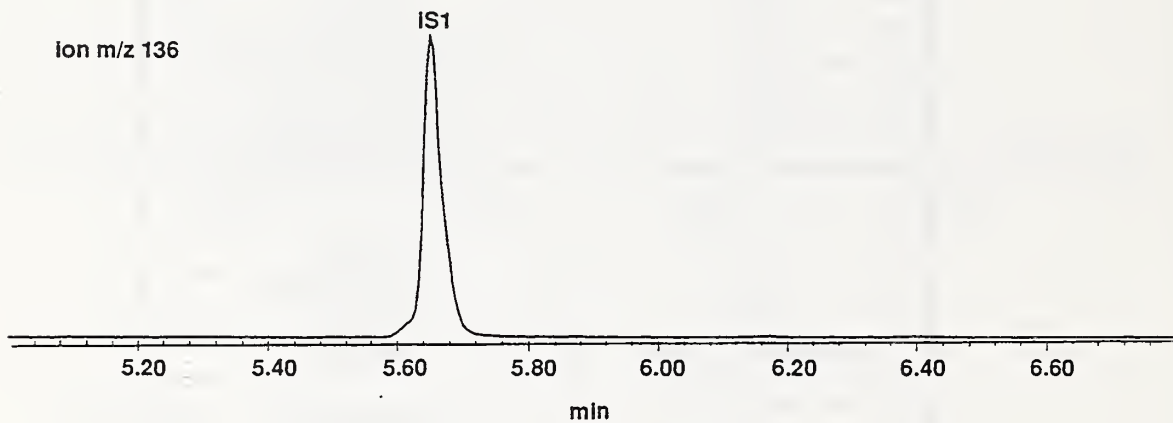
Peak Number	Polycyclic Aromatic Hydrocarbon (PAH)
4	naphthalene
IS1 (Internal Standard)	naphthalene-d ₈
2	2-methylnaphthalene
4	1-methylnaphthalene
4	biphenyl
5	acenaphthylene
9	acenaphthene
7	fluorene
IS2 (Internal Standard)	fluorene-d ₁₀
8	dibenzothiophene
IS3 (Internal Standard)	phenanthrene-d ₁₀
9	phenanthrene
10	anthracene
11	4,5-methylenephenanthrene
12	3-methylphenanthrene
13	2-methylphenanthrene
14	4- and 9-methylphenanthrene
15	1-methylphenanthrene
16	fluoranthene
17	acephenanthrylene
18	pyrene
IS4 (Internal Standard)	pyrene-d ₁₀
19	benz[a]anthracene
20	triphenylene
21	chrysene
IS5 (Internal Standard)	benz[a]anthracene-d ₁₂
22	benzo[b]- and benzo[j]fluoranthene
23	benzo[k]fluoranthene
24	benzo[a]fluoranthene
25	benzo[e]pyrene
26	benzo[a]pyrene
27	perylene
IS6 (Internal Standard)	benzo[k]fluoranthene-d ₁₂
IS7 (Internal Standard)	benzo[e]pyrene-d ₁₂
28	indeno[1,2,3-cd]pyrene
29	benzo[ghi]perylene
IS8 (Internal Standard)	benzo[ghi]perylene-d ₁₂

APPENDIX D. Reconstructed Selected-Ion Chromatograms of Teflon Filter PAH-01
Collected at the Royal Saudi Naval Base
(See Table D-1 for peak identification)

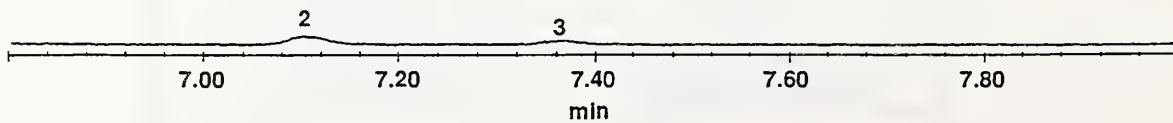
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Ion m/z 136

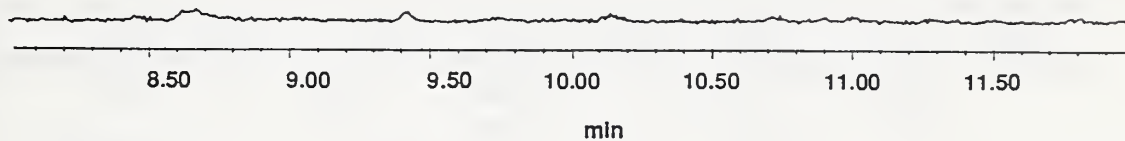


Ion m/z 142

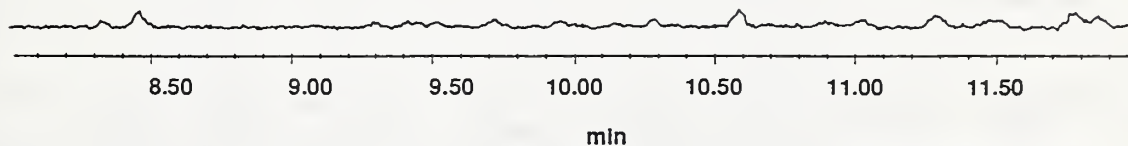


APPENDIX D. Reconstructed Selected-Ion Chromatograms of Teflon Filter PAH-01
Collected at the Royal Saudi Naval Base
(See Table D-1 for peak identification)

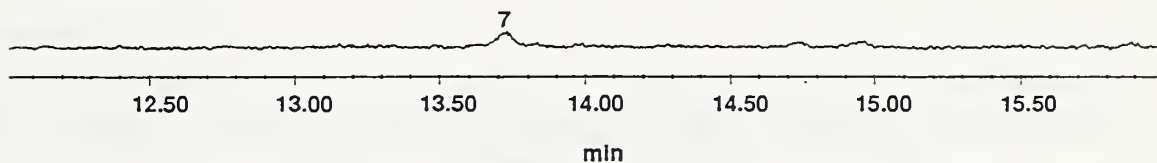
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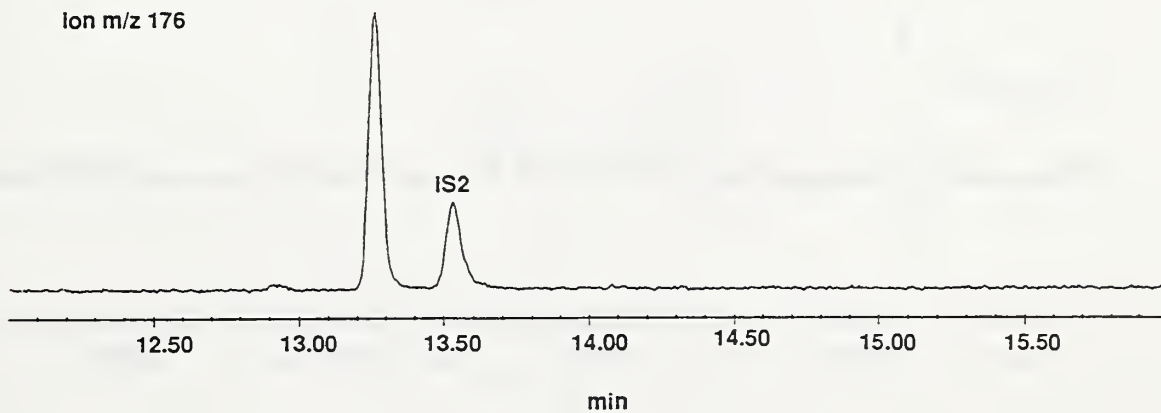
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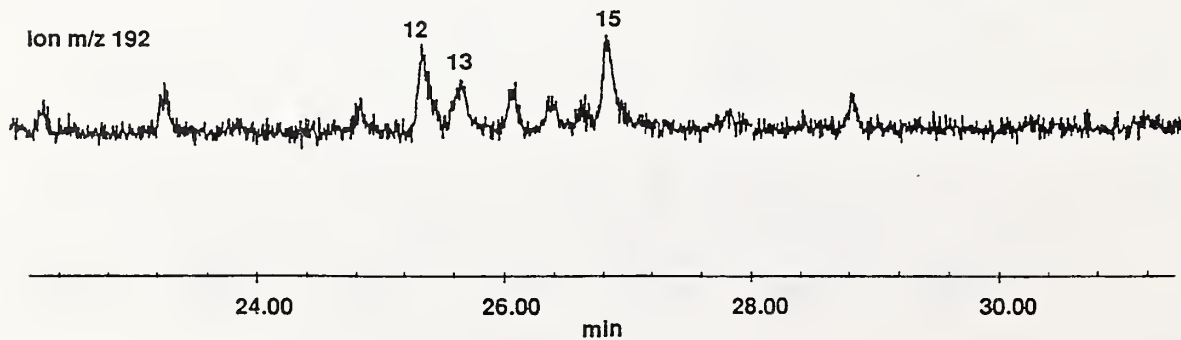
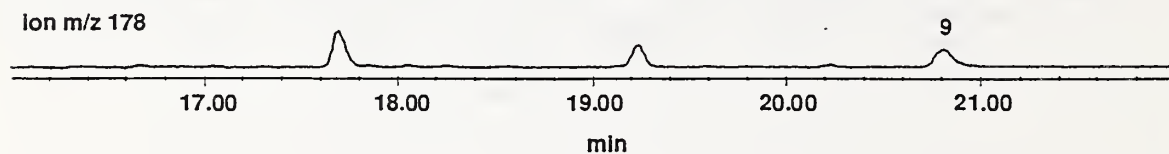
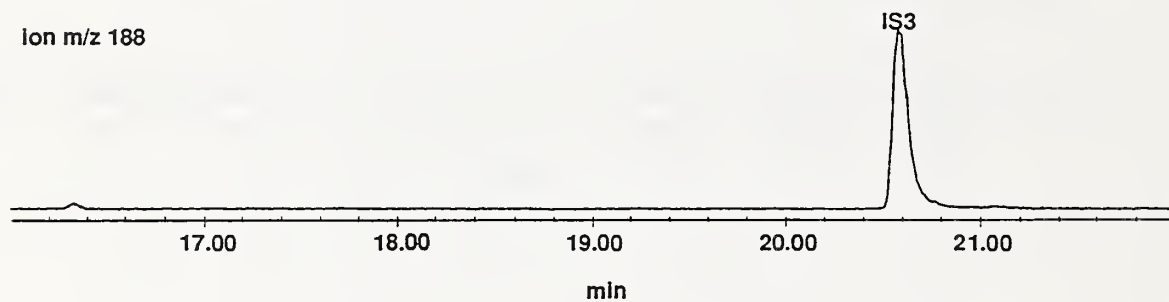
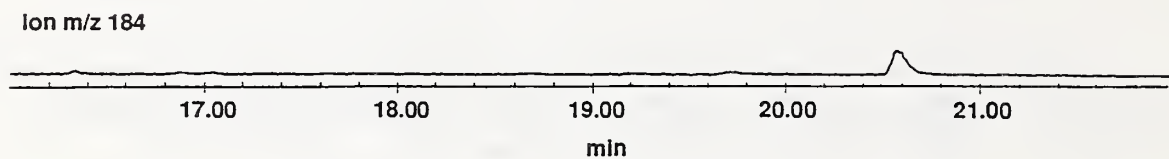
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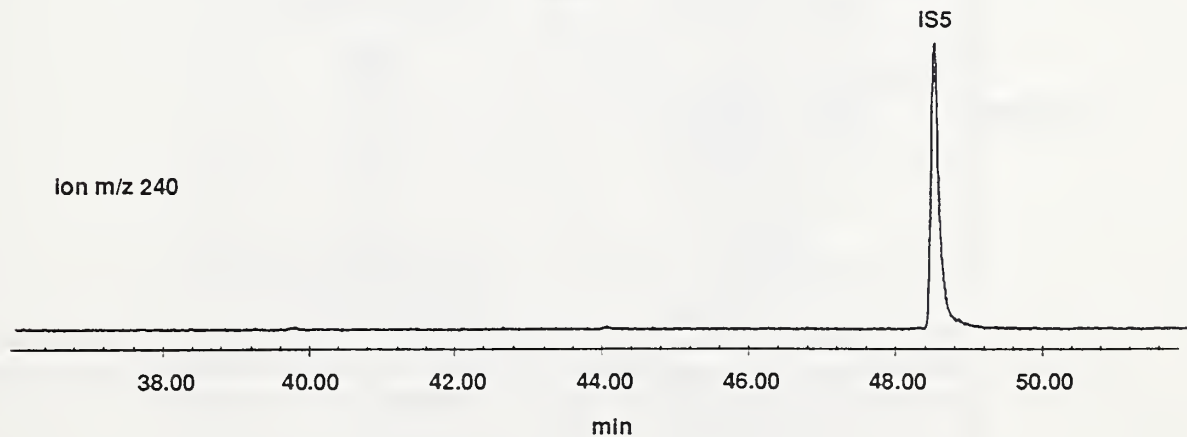
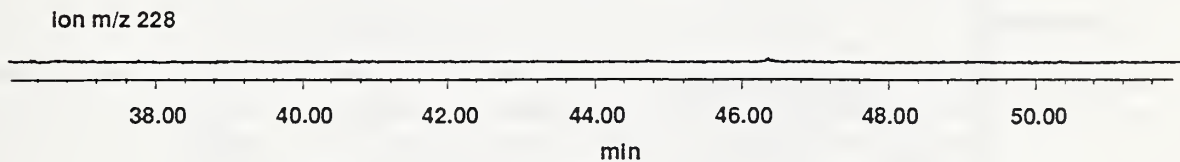
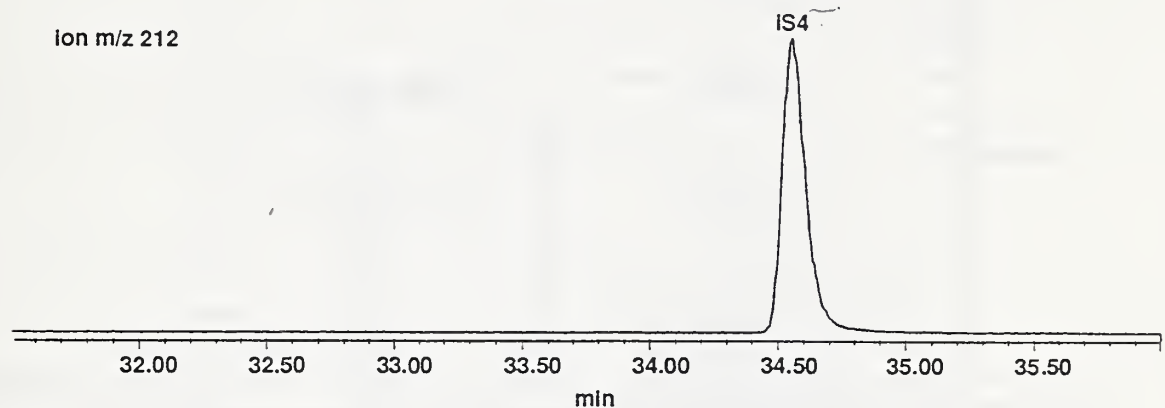
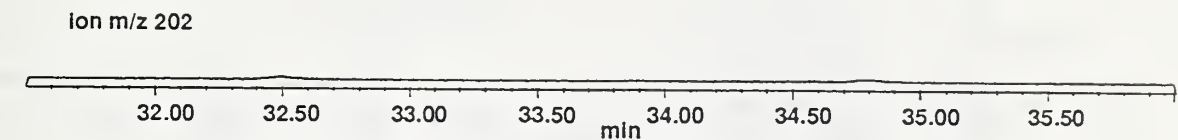
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APPENDIX D. Reconstructed Selected-Ion Chromatograms of Teflon Filter PAH-01
Collected at the Royal Saudi Naval Base
(See Table D-1 for peak identification)



APPENDIX D. Reconstructed Selected-Ion Chromatograms of Teflon Filter PAH-01
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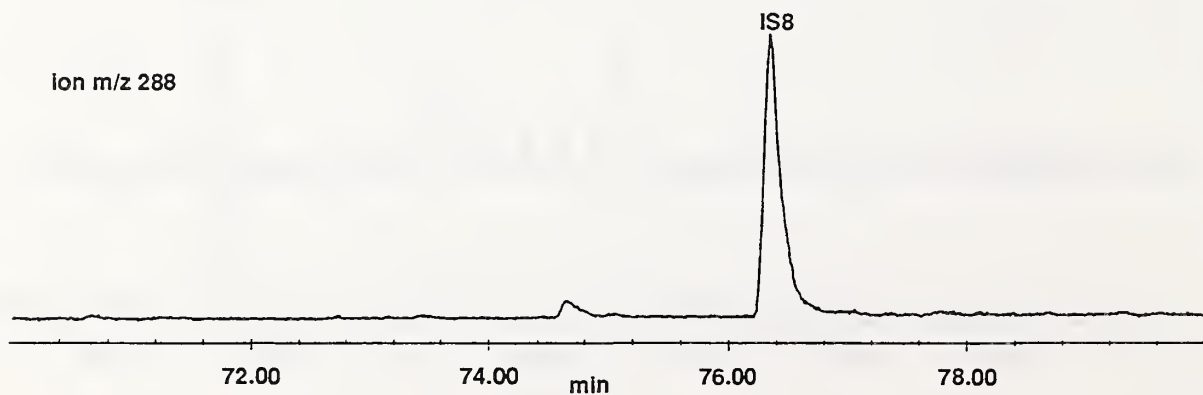
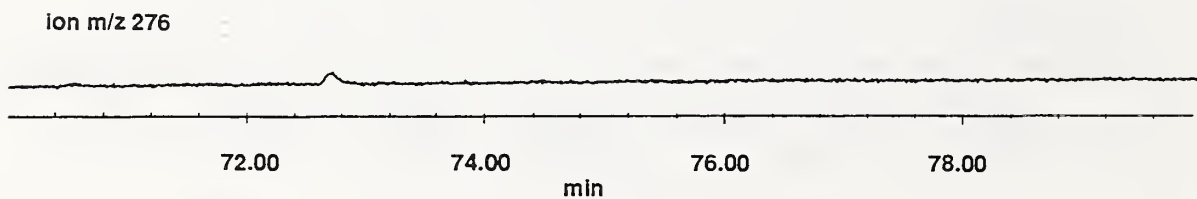
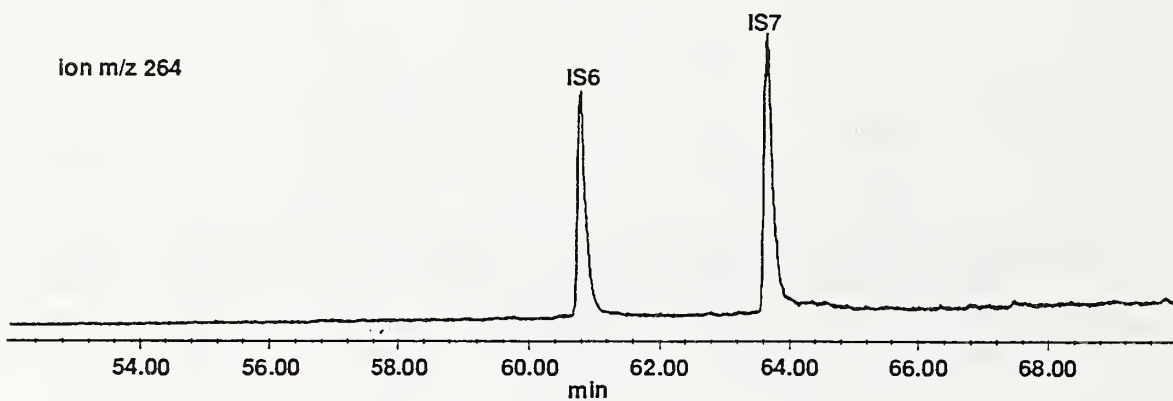
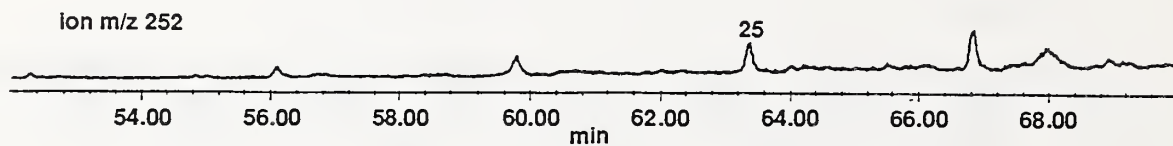


Table D-1. Peak Identifications for Reconstructed Selected-Ion Chromatograms of Teflon Filter PAH-01.

Peak Number	Polycyclic Aromatic Hydrocarbon (PAH)
1	naphthalene
IS1 (Internal Standard)	naphthalene-d ₈
2	2-methylnaphthalene
3	1-methylnaphthalene
4	biphenyl
5	acenaphthylene
6	acenaphthene
4	fluorene
IS2 (Internal Standard)	fluorene-d ₁₀
6	dibenzothiophene
IS3 (Internal Standard)	phenanthrene-d ₁₀
9	phenanthrene
10	anthracene
11	4,5-methylenepheneanthrene
10	3-methylphenanthrene
13	2-methylphenanthrene
14	4- and 9-methylphenanthrene
18	1-methylphenanthrene
16	fluoranthene
17	acephenanthrylene
18	pyrene
IS4 (Internal Standard)	pyrene-d ₁₀
19	benz[a]anthracene
20	triphenylene
21	chrysene
IS5 (Internal Standard)	benz[a]anthracene-d ₁₂
22	benzo[b]- and benzo[j]fluoranthene
23	benzo[k]fluoranthene
24	benzo[a]fluoranthene
25	benzo[e]pyrene
26	benzo[a]pyrene
27	perylene
IS6 (Internal Standard)	benzo[k]fluoranthene-d ₁₂
IS7 (Internal Standard)	benzo[e]pyrene-d ₁₂
28	indeno[1,2,3-cd]pyrene
29	benzo[ghi]perylene
IS8 (Internal Standard)	benzo[ghi]perylene-d ₁₂

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Smoke and gaseous emissions such as generated by oil-well fires impact the health of the local population. To assess the risk to public health, the chemical and physical properties of the smoke and gases must be quickly characterized. Local sampling via portable analyzers provides real-time characterization of pollutant levels. The Ground-Based Smoke Sampling Techniques Training Course and Collaborative Local Smoke Sampling project was initiated between the Ministry of Defence and Aviation (Kingdom of Saudi Arabia) and the National Institute of Standards and Technology (USA) to train Saudi medical personnel. A team of Saudi and NIST researchers collected samples in Saudi Arabia. Analysis included polycyclic aromatic hydrocarbons (PAHs), CO, CO₂ and total particulate concentrations. Split-sample analysis was conducted with some samples being analyzed in Saudi Arabia and other samples being returned to NIST for more specialized analysis, including Micro-Raman, Laser Micro-Probe, and Environmental Scanning Electron Microscopy. These analyses provide a snapshot of the physical and chemical properties of the aerosol sampled in Saudi Arabia, but the limited number of samples do not provide a reasonable basis for estimating the health risk due to exposure to smoke and gases. While these results suggest significant levels of PAH and dust, the data set is small and a program of collection and analysis of air samples in or around Saudi Arabian urban areas would provide data for determining current airborne PAH concentrations as well as for devising future air pollution control strategies. PAH concentrations were about the same order of magnitude as samples in Roanoke, Virginia, but 3 to 10 times lower than samples from Boise, Idaho. The significant concentrations of PAHs in what was expected to provide background levels indicates that a comprehensive sampling program should be implemented to characterize the PAH concentrations throughout the Kingdom.

KEY WORDS (MAXIMUM OF 9; 28 CHARACTERS AND SPACES EACH; SEPARATE WITH SEMICOLONS; ALPHABETIC ORDER; CAPITALIZE ONLY PROPER NAMES)

aerosols; environmental effects; fire research; oil spills; oil well fires; polycyclic aromatic hydrocarbons; smoke; smoke collection; smoke sampling

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